VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ
BRNO UNIVERSITY OF TECHNOLOGY

FAKULTA STROJNÍHO INŽENÝRSTVÍ
FACULTY OF MECHANICAL ENGINEERING

ÚSTAV MATERIÁLOVÝCH VĚD A INŽENÝRSTVÍ
INSTITUTE OF MATERIALS SCIENCE AND ENGINEERING

CHARAKTERIZACE NÁSTŘIKŮ DEPONOVANÝCH SUSPENZNÍM PLAZMOVÝM NANÁŠENÍM S POUŽITÍM RŮZNÝCH ORGANICKÝCH NOSIČŮ

CHARACTERIZATION OF SUSPENSION PLASMA SPRAYED COATINGS DEPOSITED USING DIFFERENT ORGANIC CARRIERS

BAKALÁŘSKÁ PRÁCE
BACHELOR'S THESIS

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BRNO 2019

VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ FAKULTA STROJNÍHO INŽENÝRSTVÍ

Bachelor thesis assignment

Institute:	Institute of Materials Science and Engineering
Student:	**Daniel Dukovský**
Study program:	Mechanical Engineering
Field of study:	Fundamentals of Mechanical Engineering
Supervisor:	**Ing. Jan Čížek, Ph.D.**
Academic Year:	2018/19

In accordance with Act No. 111/1998 on universities, the study and examination regulations of the Brno University of Technology, the director of the Institute determines the following topic of the bachelor thesis:

Characterization of suspension plasma sprayed coatings deposited using different organic carriers

Characteristics of the task:

Considering the technological advances in thermal spraying, one of the focal points in the last few years was related to suspension spraying. The method allows completely avoiding the drawbacks associated with spraying from powder feedstock and enables formation of nanostructured materials, thereby opening a new application niche. As proved in the literature, the properties of organic compound used for such suspensions (typically ethanol) have a major impact on the final coating characteristics and qualities. The aim of the thesis is formation of suspensions of a selected ceramic material (Al2O3) having different organic solvents (ethanol and Dowanol), deposition of coatings using a unique, hybrid water-stabilized plasma torch, and analyses of the deposits.

Goals of bachelor thesis:

- to familiarize the student with the thermal spray processes
- to familiarize the student with the suspension routes and its respective advantages
- to deposit coatings of a supplied ceramic material (Al2O3) using two different organic solvents (etanol, Dowanol)
- to characterize the coatings in terms of deposition efficiency, microstructure, and phase and element composition

List of recommended literature:

PAWLOWSKI Lech. Suspension and solution thermal spray coatings. Surface and Coatings Technology, 2009. Vol. 203(19), pp. 2807-2829.

FAN, Wenjuan and Yu BAI. Review of suspension and solution precursor plasma sprayed thermal barrier coatings. Ceramics International, 2016. Vol. 42(13), pp. 14299-14312.

TESAR, T., R. MUSALEK, J. MEDRICKY, J. KOTLAN, F. LUKAC, Z. PALA, P. CTIBOR, T. CHRASKA, S. HOUDKOVA, V. RIMAL and N. CURRY. Development of suspension plasma sprayed alumina coatings with high enthalpy plasma torch. Surface and Coatings Technology, 2017. Vol. 325, pp. 277-288.

The date of consignment of the bachelor thesis is set by the schedule of the academic year 2018/19

In Brno

L. S.

prof. Ing. Ivo Dlouhý, CSc. Director of the Institute	doc. Ing. Jaroslav Katolický, Ph.D. Dean of the Faculty

Abstrakt
Cílem této bakalářské práce bylo charakterizovat a porovnat povlaky nanesené plazmovým žárovým nanášením ze suspenze s použitím různých organických nosičů. Teoretická část obsahuje stručný popis běžně používaných metod žárového nanášení a blíže se věnuje technologii hybridního vodou stabilizovaného plazmatu (hořák s touto technologií byl využit pro nanesení povlaků v tomto výzkumu). Druhá polovina teoretické části se zabývá věcným popisem povlaků a metodami nanášení prášku o velikosti částic v řádu nanometrů, kde hraje důležitou roli právě použití suspenze. Experimentální část je zaměřena na vliv použitého solventu v suspenzi na charakteristiky výsledného povlaku. V závěrečné části jsou prezentována a diskutována naměřená data a vyhodnoceny výsledky.

Abstract
The aim of this bachelor thesis was to characterize suspension plasma sprayed coatings deposited using different organic carriers. The theoretical part contains a brief description of common thermal spray methods and closely describes hybrid water stabilised plasma technology used for the deposition of coatings in this research. Further, it deals with the factual description of coatings and methods of application of powder with nano-sized particles using the deposition from suspension. The experimental part is focused on the influence of a selected solvent in suspension on the resulting coating. Measured data and evaluated results are presented and discussed in the final part.

Klíčová slova
Žárové nanášení, suspenze, povlak

Keywords
Thermal spray, suspension, coating

DUKOVSKÝ, D. *Charakterizace nástřiků doponovaných suspenzním plazmovým nanášením s použitím různých organických nosičů.* Brno: Vysoké učení technické v Brně, Fakulta strojního inženýrství, 2019. 54 s. Vedoucí bakalářské práce Ing. Jan Čížek, Ph.D.

Rozšířený abstrakt

Za posledních 100 let bylo vyvinuto a zdokonaleno mnoho metod materiálových úprav k dosažení co nejlepších technických vlastností použitého materiálu. Každá z nich má přitom jiný přístup a úhel pohledu na úpravu součásti. Téma této bakalářské práce se věnuje problematice úprav materiálu pomocí metod povrchového inženýrství. Jednou z metodik v této oblasti je depozice povlaků, které hrají významnou a nezastupitelnou roli v modifikaci vlastností materiálu. Jejich hlavní výhodou je zvýšení kvality povrchu a přidání vlastností, které původní materiál postrádá.

Povlakové vrstvy nanášené metodami žárového nanášení vznikají depozicí z práškových materiálů a v posledních letech i ze suspenzí, jejichž předností je možnost nanášet prášek o velikosti částic v řádech nanometrů. Suspenze jsou tedy směsí tekutého nosiče (solventu) a nanočásticového prášku. Nosiče použité v suspenzích tohoto výzkumu mají různá chemická složení, viskozitu, molární hmotnost, rychlost odpařování a tedy i chemický účinek na práškovou přísadu. Všechny tyto parametry by následně měly mít vliv na kvalitu a vlastnosti finálního povlaku. Jak vyznamný je tento vliv je předmětem zkoumání této práce.

Tato práce se zaměřuje na žárově nanášené povlaky ze dvou suspenzí, které se liší použitými solventy. Pro srovnání vlivu solventu na nanesený povlak byly vytvořeny suspenze z keramického prášku Al_2O_3 o koncentraci 10 $hm.\%$ a solventu v podobě etanolu (CH_3CH_2OH) v jednom případě a dowanolu ($CH_3O[CH_2CH(CH_3)O]_2H$) v případě druhém. Jaký vliv má různá koncentrace pevné složky v solventu na výsledný povlak, bylo zkoumáno porovnáním se třetí suspenzí tvořenou 20 $hm.\%$ Al_2O_3 v dowanolu.

Suspenze byly vytvořeny navážením a smícháním solventu s povlakovým materiálem a disperzním činidlem. Před samotným nanášením byla změřena viskozita připravených suspenzí a získané výsledky byly použity pro nastavení podávacích vzdáleností při vlastní pozdější depozici. Vzniklá suspenze byla pak nejméně dvacet minut před stříkáním důkladně promíchána a přefiltrována skrze síto 125 μm pro odstranění případných nečistot. Suspenze byla poté přemístěna do speciálně vyvinutého podavače, ze kterého byla dále dávkována do plazmatu. V podavači byla suspenze neustále agitována, aby nedocházelo k sedimentaci částic.

Pro deponování suspenze byla zvolena metoda žárového nanášení, konkrétně technologie hybridního vodou stabilizovaného plazmatu vyvinutého na Ústavu fyziky plazmatu AV ČR v Praze. Nastavení hořáku, úhlu podávání suspenze, nanášecí vzdálenosti a nanášecí teploty bylo upraveno na základě předchozích zkušeností s podobnými suspenzemi podle snímků z termokamer (shadowgraphy). Suspenze byly nanášeny na dva typy substrátu - konstrukční ocel S235 a korozivzdorná ocel SS304 - za předpokladu, že i samotný substrát bude mít vliv na vzniklý povlak. Substráty byly otryskány a zbaveny nečistot ponořením do acetonu v ultrazvuku. Takto připravené kusy byly připevněny na karusel a přichystány k depozici. Z důvodu dalších měření byly použity substráty jak obdélníkové 20x30 mm^2, tak kruhové o průměru 25 mm.

Vzorky byly zváženy před a po depozici, stejně tak byla změřena i jejich tloušťka k určení depoziční efektivity. Kruhové vzorky byly použity na odtrhovou zkoušku přilnavosti, kde byly přilepeny ke zkušebním tělesům a dále testovány dle normy ASTM C-633. Pro všechna ostatní měření byly použity vzorky obdelníkové.

Po depozici byly vzorky testovány na povrchovou drsnost a podrobeny XRD analýze. Následně byly rozříznuty a zality do pryskyřice a připraveny pro další výzkum. Vytvrzené špunty se vzorky byly sbroušeny a vyleštěny. Bylo tak možné s nimi dále pracovat

v mikrotvrdoměru a v rastrovacím elektronovém mikroskopu, kde byly pořízeny snímky o různých zvětšeních. Ze snímků při zvětšení 3000x byla stanovena porozita pomocí softwaru ImageJ.

Z výsledků bylo zřetelné, že oba solventy mají pozorovatelné výhody i nevýhody a jejich existence tak prokázala jednoznačný vliv organického nosiče na vlastnosti deponovaného povlaku. Naměřená data dále potvrdila, že téměř ve všech případech byly dowanolové suspenze lepší. Povlaky byly tvrdší, méně porézní a obsahovaly více stabilní fáze $\alpha - Al_2O_3$. Po zvážení a přeměření tloušťky povlakovaných vzorků, stejně tak, jako po vizuálním srovnání mikroskopových snímků, byla potvrzena i vyšší depoziční efektivita. Nicméně odtrhová zkouška odhalila i nedostatky tohoto solventu oproti etanolu. Naměřené hodnoty adheze a koheze povlaku byly téměř poloviční než hodnoty, jichž dosáhly povlaky z etanolové suspenze.

Celkově však dowanol prokázal své kvality a jeho užití má v dané oblasti smysl. Je vhodný zejména pro aplikace, kde jsou nároky na vyšší tvrdost, nebo efektivnější depozici a tím i snížení výrobních nákladů. Není však vhodný pro součásti vyžadující vyšší přilnavost a soudržnost povlaku, kterou splňuje etanol.

Prohlašuji, že jsem bakalářskou práci na téma *Charakterizace nástřiků deponovaných suspenzním plazmovým nanášením s použitím různých organických nosičů* vypracoval samostatně pod vedením pana Ing. Jana Čížka, Ph.D. a použil jsem pouze uvedené prameny a literaturu.

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Daniel Dukovský

May 24, 2019

Touto cestou bych rád poděkoval svému vedoucímu bakalářské práce panu Ing. Janu Čížkovi, Ph.D. za jeho vřelý a přátelský přístup. Též si cením velké ochoty a pomoci všech zúčastněných z Ústavu fyziky plasmatu při realizaci celého výzkumu, jmenovitě Ing. Tomáš Tesař, Ing. Radek Mušálek, Ph.D., Ing. Jakub Klečka, Ing. Jan Medřický a Ing. Marek Janata. V neposlední řadě patří poděkování především mým rodičům, kteří mě podporovali po celou dobu studia.

Daniel Dukovský

Contents

1 Introduction

Many methods of material modifications have been developed and perfected over the past hundred years to achieve the best possible technical properties of the used materials.

The topic of this bachelor thesis belongs to surface engineering methods. These methods deal with the application of coatings that play a significant and irreplaceable role in the modifications of material. Their main benefit is enhancing surface quality and adding properties that the original material does not have.

This work is focused on coatings deposition from different suspensions using thermal spray method. Using the suspension entails many benefits over the deposition from powder. The specific aim of this research is to prove the impact of the organic carrier on the resulting coating. Ethanol and dowanol were chosen as solvents to compare suspensions' properties. Both carriers used in suspensions have different chemical compositions, the evaporation rate as well as the chemical effect on the powder additive so it is possible to assume different properties of the deposited coatings.

2 Thermal spray deposition

This chapter discusses thermal spray methods, their use and differences. Further, it provides a more detailed information on the most common thermal spray technologies, particularly plasma spraying as a method used in the experimental part of this work.

2.1 General description

These days there are many different technologies of material and surface modifications. Each of them has its pros and cons. Also their approach is different, they differ in methods of modifying the surface, techniques they use, and influence on the substrate. Mechanical finishing is a way of plastic deformation of component's surface, such as burnishing or peening. Another approach is removing and reshaping of surface, and that means grinding, polishing, or abrasive blasting. Last more substantial category is adding and altering [1].

This category belongs to the area of surface engineering divided in two subcategories. The first one deals with modification of already existing material, while formation of a new layer onto the surface of component belongs to the second subcategory. First subcategory contains carburizing or nitriding processes and they differ from thermal spray because the additive (carbon or nitrogen) is saturated into thin layer in the surface of component, while PVD, CVD, or thermal spray create a layer of material on the surface of component [2][3].

Thermal spray method history goes back to the 19th century with first thought of spraying liquid metal [4]. Thermal spray technology has been developed for coating applications that provide functional surfaces to protect or improve performance of a substrate or component. The most valid difference between thermal spray and other coating processes is in size of sprayed particles and therefore in thickness of applied layer. While the other methods such as CVD, PVD, or sputtering may deposit material onto surfaces as individual ion, atoms, or molecules, thermal spray methods operate with droplets of molten material spanning up to 100 μm in diameter and those are massive particles compared to atoms or molecules. Therefore, the layer deposited with thermal spray is thicker and non-homogeneous and provides protection from corrosion, wear, and heat [1]. The comparison of coatings thickness is shown in the Table 1 and Fig. 2.1 shows the schematic deposition and coating content of thermal spray.

Table 1: Comparison of coating thickness of selected surface modification technologies [5]

Coating process	**Typical coating thickness**
Thermal spray	40 - 3000 μm
PVD	1 - 5 μm
CVD	1 - 50 μm
Galvanizing	1 - 5 μm

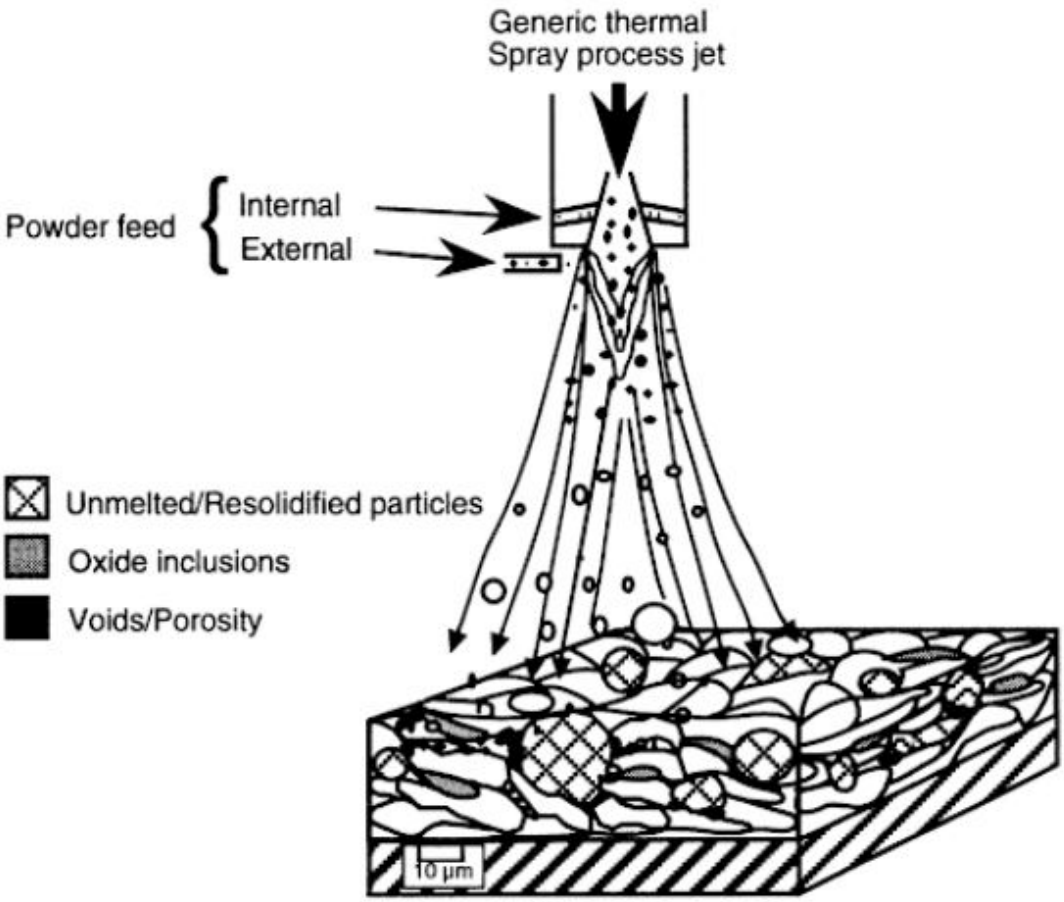

Figure 2.1: Schematic of thermal spray deposition from powder feedstock [1]

2.2 Thermal spray methods

Nowadays thermal spray is process grouped in three major categories: flame spray, electric arc spray, and plasma arc spray. These energy sources are supposed to heat and melt the coating material (in pure form of powder, wire or rod, or in mixture such as suspension or solution) [1].

Thermal spray as a technology was developed to cover surfaces with metallic or non-metallic (e.g. ceramic) material to prevent undesirable effects from environs and improve the whole scale of component's properties, such as mechanical, electrical, thermal, corrosion and or erosion properties. Methods used for thermal spray are shown in Fig. 2.2. Some of these methods are provided in more detail in this section. A standalone section is then devoted to plasma spraying as a technology used in this work.

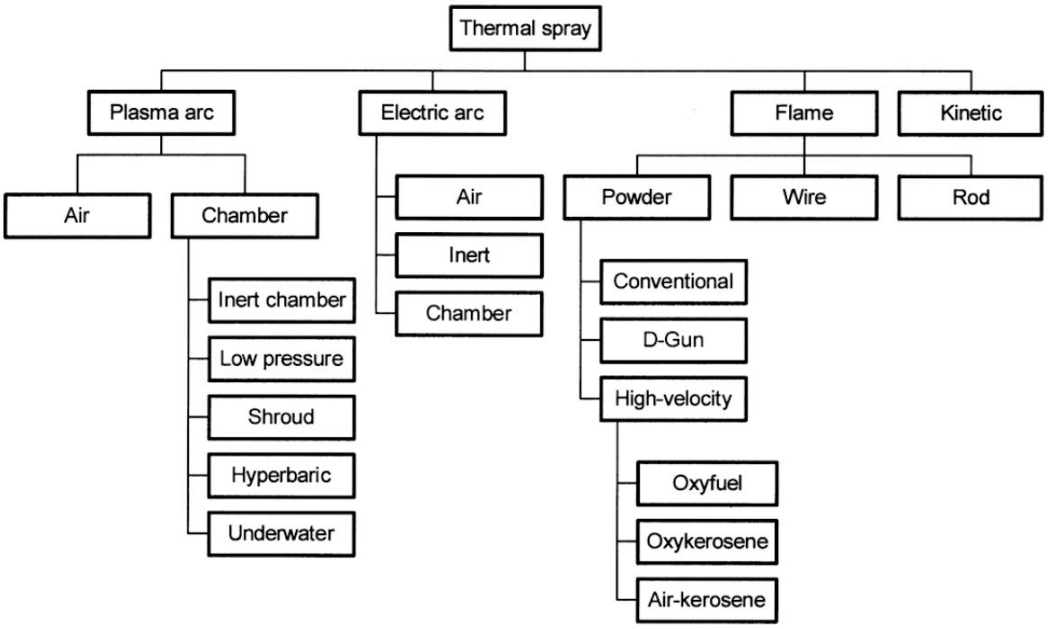

Figure 2.2: Thermal spray processes and subsets [6]

2.2.1 Flame spraying

- **Conventional flame spraying**

  Flame spraying, is the oldest of the thermal spraying processes (scheme is shown in Fig. 2.3). Its most significant advantage is low capital investment, high deposition rate of coating material and relatively easy operation. Flame spray uses combustible gas as a heat source to melt the coating material. Additive materials can be deposited in rod, wire, or powder form. Vast majority of components are sprayed manually. Most flame spray guns can be adapted to use several combinations of gases to balance operating costs and coating properties. Acetylene, propane, methyl–acetylene–propadiene (MAPP) gas, and hydrogen are commonly used flame spray fuel gases. Flame temperatures and characteristics depend on the oxygen-to-fuel gas ratio and pressure [5][6].

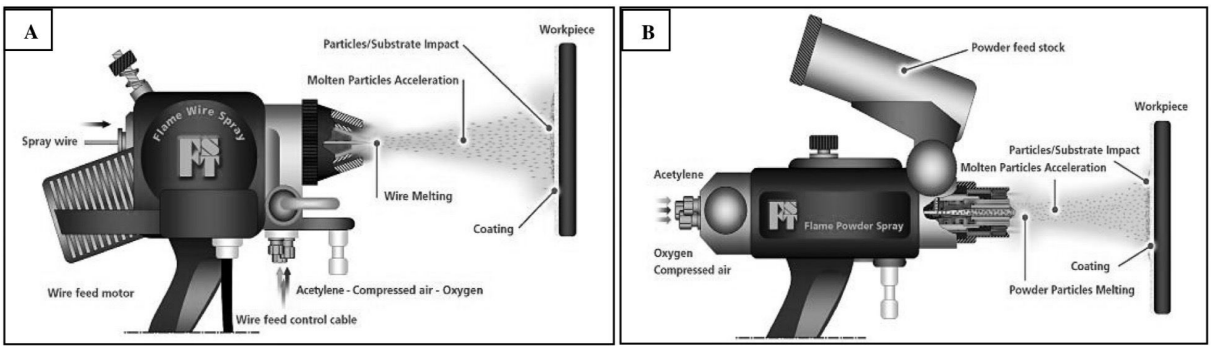

Figure 2.3: Scheme of (A) wire flame and (B) powder flame spraying processes [6]

- **D-Gun**

  Detonation gun (D-Gun) spraying is a thermal spray coating process, which provides extremely good adhesive strength, low porosity and compressive residual stresses in coating surface. Combustion mixture consists of oxygen and acetylene that are fed through a tubular barrel closed at one end. In order to prevent the possible back firing a blanket of nitrogen gas is allowed to cover the gas inlets. Simultaneously, the coating powder is fed into the combustion chamber. The gas mixture inside the chamber is ignited by a simple spark plug. The combustion of the gas mixture generates high pressure shock waves (detonation wave), which then propagate through the gas stream. Depending upon the ratio of the combustion gases, the temperature of the hot gas stream can go up to 4000 $°C$ and the velocity of the shock wave can reach 3500 m/s [8]. If the spray parameters are properly adjusted, the powder particles temperature does not exceed the melting point temperature and the sprayed particles are slightly soft [7]. The high kinetic energy of the hot powder particles on impact with the substrate form very dense and strong coating. The coating thickness depends on the ratio of combustion gases, powder particle size, carrier gas flow rate, frequency and distance between the barrel end and the substrate. The chamber is further flushed with nitrogen again to remove all the remaining "hot" powder particles from the chamber. With this, one detonation cycle is completed and repeated until the required thickness of coating is deposited [8]. Scheme of detonation gun is pictured in Fig. 2.4.

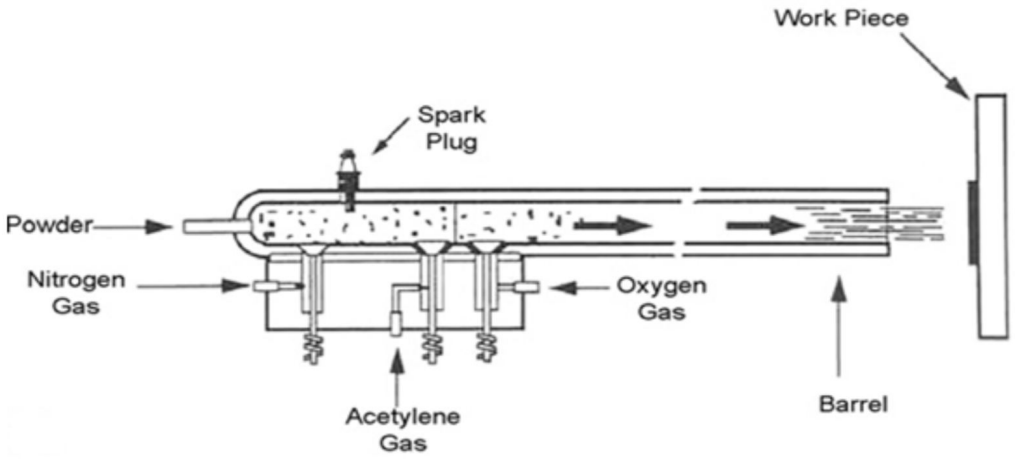

Figure 2.4: Scheme of detonation gun thermal spray method [9]

- **HVOF**

  Union Carbide (Texas, USA) first introduced the high velocity oxygen fuel (HVOF) process in 1958. Since then HVOF has brought significant development to the field of thermal spray coating [10]. HVOF thermal spray processes are coating techniques for depositing wear- and corrosion-resistant layers for a variety of industrial applications including e.g. ball valves in the petrochemical and mining sectors, steelmaking and paper-making rolls, internal combustion engine parts, hydraulic and pneumatic components (including landing gear parts), etc. This method (shown

in Fig. 2.5) uses a supersonic stream of hot gas that is formed by expanding the products of a high-pressure, oxy-fuel combustion (combination of oxygen with various fuel gases including hydrogen, propane, propylene, hydrogen and even kerosene) through a suitable nozzle. The flame temperature varies in the range of 2500 $°C$ to 3200 $°C$, depending on the fuel, the fuel gas/oxygen ratio and the gas pressure. Powder particles, injected into this stream, are heated and accelerated to very high velocities, so that, upon impacting onto the substrate, they bond tightly, producing a dense layer with good adhesive and cohesive strength [11].

The ability to produce dense coatings with low amount of degradation, oxidation of metallic materials, and phase transformations is the main advantage of the HVOF process. This is due to the short dwell time of the particles in a relatively cold flame. It is widely used to produce cermet and metal coatings, but the HVOF process has also been demonstrated to be able to deposit dense ceramic coatings. However the drawback of this technique is that coating is not 100% crystalline [6][11].

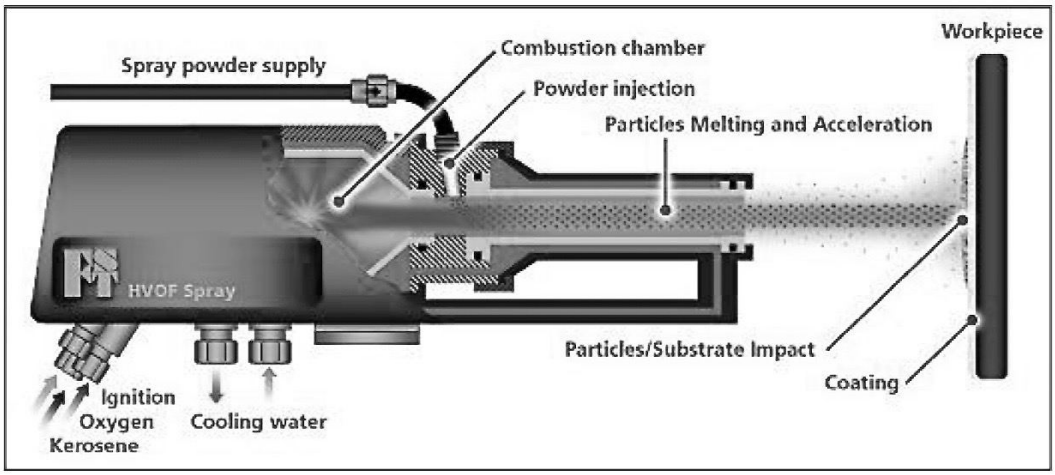

Figure 2.5: Scheme of high velocity oxygen-fuel thermal spray method [6]

2.2.2 Electric arc spraying

Typically, a pair of wires are melted by an electric arc in the electric arc spray process. The molten material is atomised and propelled towards the substrate surface by compressed air. It is energy efficient due to all of the input energy used to melt the added material. The impacting molten particles on the substrate solidify to form a coating. This process keeps the substrate temperature low because there is no hot jet of gas, so it can avoid damage, metallurgical changes and distortion of the substrate material. Electric arc spray coatings are normally denser and stronger than their equivalent combustion spray coatings. Low running costs, high spray rates and efficiency make it convenient for spraying large areas and high production rates. The main disadvantage of the electric arc spraying is that only electrically conductive wires can be sprayed. And also if substrate preheating is required, a separate heating source is needed. The usual applications of this process are anti-corrosion coatings of zinc and aluminium and machine element work on large components [6][12]. The process of electric arc spray is shown in Fig. 2.6.

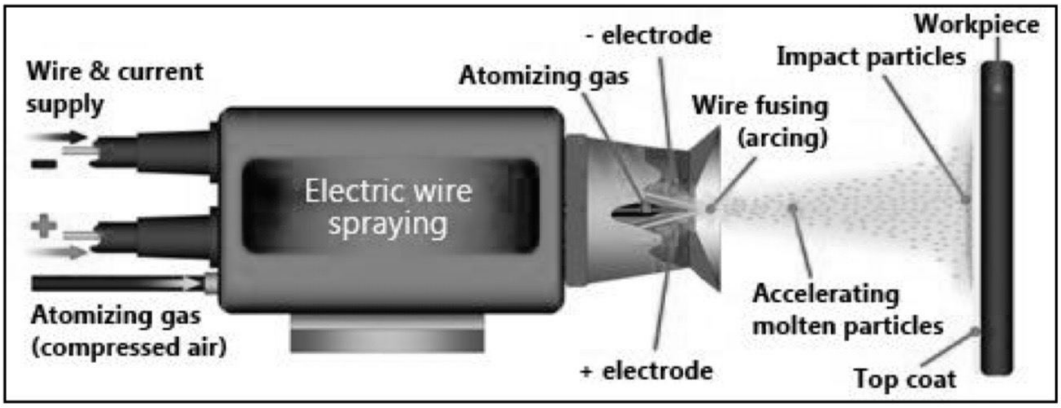

Figure 2.6: Scheme of electric arc spray process [6]

2.2.3 Plasma spraying

The plasma spray was used as a depositing technology in this research. This is why it is going to be described more extensively and own section will be given to the special type of thermal spray (WSP-H) used for the experiment. Figure 2.7 shows scheme of plasma spray process

The plasma spray gun comprises a water cooled copper anode and tungsten cathode. Gas-stabilized plasma sources are commonly used to create a plasma, usually from argon, nitrogen, hydrogen, or helium. Alternatively, water can be used as the plasma-forming medium (water-stabilized plasma sources) or, eventually, a combination of water and argon. The plasma is initiated by a high voltage discharge which causes localised ionisation and a conductive path for a DC arc to form between cathode and anode. The resistance heating from the arc causes the gas to reach extreme temperatures, dissociate and ionise to form a plasma. The plasma exits the nozzle as a free or neutral plasma flame (plasma which does not carry electric current). Cold gas around the surface of the water cooled anode nozzle being electrically non-conductive constricts the plasma arc, raising its temperature and velocity. Powder or recently a suspension composed of powder and liquid carrier (solvent) is fed into the plasma flame most commonly via an external port mounted near the anode nozzle exit. The powder or suspension is so rapidly heated and accelerated that spray distances can be 25 - 150 mm [13].

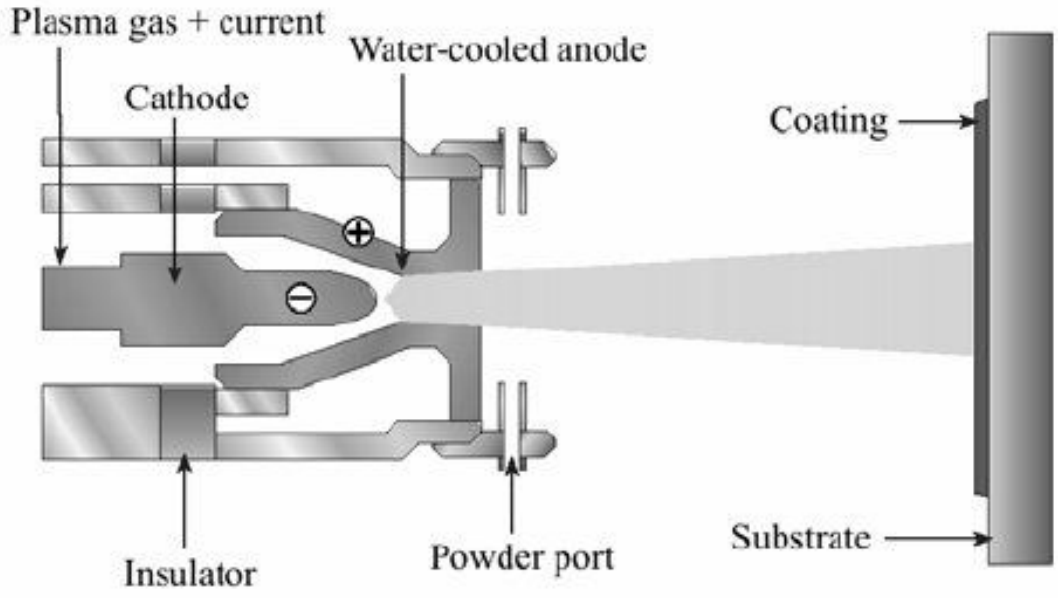

Figure 2.7: Scheme of plasma spray process [14]

The plasma spray process is most commonly used in normal atmospheric conditions and referred as APS (atmospheric plasma spray). Some plasma spraying is conducted in protective environments using vacuum chambers filled with a protective gas at low pressure, this is referred as VPS (vacuum plasma spray) or LPPS (low pressure plasma spray). Plasma spraying has the advantage of being able to spray very high melting point materials like ceramics such as alumina or zirconia. Table 2 shows a comparison of several coating processes especially focused on different heat conditions and coatings properties. Plasma sprayed coatings are generally much denser and stronger than the other thermal spray processes with the exception of HVOF, HVAF and cold spray processes. Plasma spray coatings account for the widest range of thermal spray coatings and applications which makes this process the most versatile. On the other hand, high fuel costs and complexity of process are disadvantage of plasma spray [13]. This problem can be partly solved using WSP-H which reduces the costs to the minimum.

Table 2: Comparison of thermal spray processes [6]

Process	**Material form**	**Flame temperature** $[^{\circ}C]$	**Gas velocity** $[m/s]$	**Porosity** [%]	**Adhesion** $[MPa]$
Plasma spray	Powder	12000 - 16000	500 - 600	2 - 5	40 - 70
Wire arc spray	Wire	5000 - 6000	<300	5 - 10	28 - 41
Wire flame spray	Wire	3000	<300	5 - 10	14 - 21
HVOF	Powder	3200	1200	1 - 2	70>

2.3 Hybrid water-stabilised plasma

This chapter is dedicated to water/gas stabilised plasma utilised for experiments in the study. Most of the plasma torches available today use only gas flow to stabilise the arc. The plasma power is then limited by gas flowing and protecting the arc chamber walls from overloading. Usual temperatures achieve 6000 K to 14000 K and plasma enthalpy reaches 1 to 100 MJ/kg [15].

First water-stabilised plasma trials were undertaken in 1920s by Gerdien and Lotz [16]. More experiments with the electric arc stabilised with arc column by water vortex were executed in the middle of 20th century [17]. Plasma torches with water stabilisation reached and still reach much higher temperatures and enthalpies than common gas stabilized plasma torches. The temperatures cross maximum about 50000 K and the enthalpy approaches nearly 300 MJ/kg. On the other hand, water-stabilised plasma torches exhibit a rather low plasma flow rates which is benefit of gas-stabilised plasma [15].

Principle of stabilisation of plasma by water is shown in Fig. 2.8. Electric arc is ignited in the centre of water vortex which is created with tangential injection of water into the chamber and then diverted into the outlet. Energy dissipated in the arc is transported to the inner surface of water vortex where evaporation, heating and ionisation of vapour are occurred [15]. Those are fundamental mechanisms of producing plasma using a liquid medium.

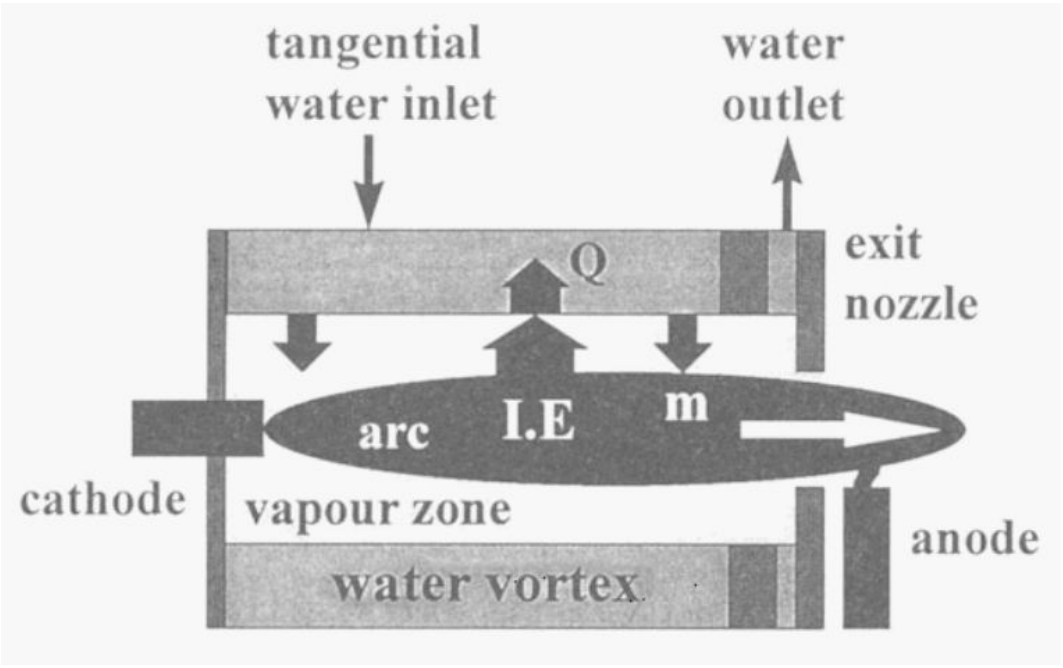

Figure 2.8: Schematic of water-stabilised plasma [15]

Current gas-stabilised plasma torches reach similar arc powers as water-stabilised plasma torches do, but their handicap is large consumption of gas media that is expensive. The problem with excessive costs on gas medium and low plasma flow rate is solved by hybrid water/gas-stabilised plasma (WSP-H).

The technology of plasma stabilised by combination of water and gas is unique and takes advantages of both media. WSP-H combines high enthalpy and arc power (range 90 kW - 200 kW) of water-stabilised plasma with increased plasma flow rate and density of gas-stabilised plasma [18].

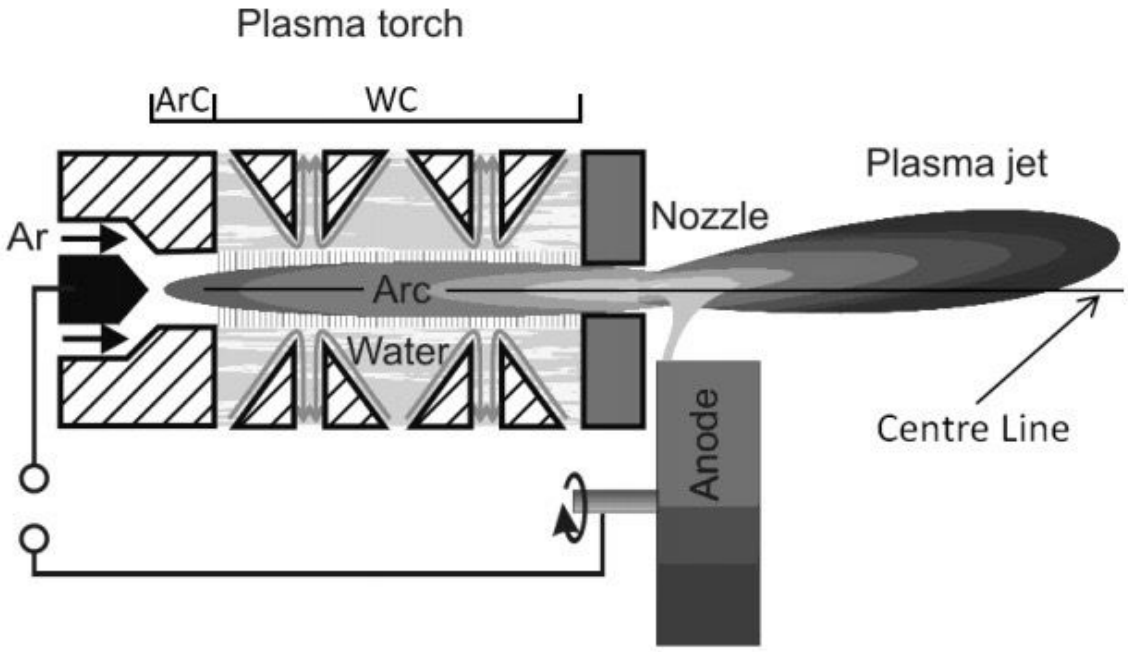

Figure 2.9: Schematic of hybrid water-stabilised plasma torch [19]

WSP-H using water as a liquid medium and argon as a gaseous one for stabilisation disposes with arc power from 22 to 150 kW and plasma temperatures from 14000 K to 22000 K [18].

Figure 2.9 shows the principle of functioning of WSP-H. The arc chamber is divided into two parts. Firstly, the gas (usually argon or mixtures of argon with hydrogen or nitrogen) enters a short cathode part of chamber along the tungsten cathode tip where the arc is stabilised by a tangential gas flow. Then it continues to a longer part of chamber where the arc is stabilised with water vortex [19]. The arc column stabilised by a direct contact with water vortex is referred as Gerdien arc with features such as very high plasma temperatures and high intensity of short-wave ultra-violet radiation [20]. This arrangement allows the additional stabilisation of cathode area and provides a new possibility of wider range of controlling the plasma jet. The WSP-H torch is equipped with water-cooled revolving disk anode externally placed in front of the nozzle exit [18]. This concept of positioning and rotating the anode was created because of the high temperature plasma that quickly degrades and eventually destroys the anode's material.

3 Coating feedstock

Coatings do not play only an aesthetic role in technical practice but, more importantly, they provide functional properties. The basic substance of thermal spray coatings is powder, usually in raw form or mixed with other substance and thus creating a mixture such as suspension or solution. Table 3 provides characteristics and example applications of commonly sprayed powders using thermal spray.

Table 3: Thermal spray materials and their applications [5]

Powder material	**Typical alloy**	**Characteristics**	**Application**
Pure metals	Zn	Corrosion protection	Bridge construction
Self-fluxing alloys	$FeNiBSi$	High hardness, fused minimal porosity	Shafts, bearings
Steel	$Fe_{13}Cr$	Economical, wear resistance	Repair
NiCrAlY	$NiCrAlY$	High temperature corrosion resistance	Gas turbine blades
Nickel-graphite	$Ni_{25}C$	Anti-fretting	Compressor inlet ducts
Oxides	Al_2O_3	Oxidation resistance, high hardness	Textile industry
Carbides	$WC_{12}Co$	Wear resistance	Shafts

3.1 Aluminium oxide powder

Alumina or Al_2O_3 was powder used in the experiment and a more detailed description is desirable. It is a polymorphic compound and may create, as many others, several different crystalline lattices. The alumina deposits consist several meta-stable crystallographic modifications and only one is stable and offers suitable mechanical properties to use [21]. This state is referred to as the α-Al_2O_3. The polycrystalline lattice has large oxygen ions with arrangement A–B–A–B and forms the HCP sublattice [22]. This stable phase is desirable in final coating for its high hardness and corrosion resistance but thermal spraying generally forms coatings with high content of meta-stable γ and δ phases because of the rapid cooling of the deposited material [23]. This undesirable effect can be subsequently reversed by heating the coating to elevated temperatures and increase the α-phase content [21].

The nano-size alumina powder with high content of α-phase is not so easy to obtain. However, there are methods such as sol-gel [24][25], hydrothermal [26], coprecipitation, mechanical milling, vapor-phase reaction and combustion [27], which can produce this ultra-fine powder. According Mirjalili et al. [28], the sol-gel synthesis provides relatively inexpensive process and thus become an effective method of producing nano-size alumina.

3.2 Solutions and suspensions

Recently, the coatings with nano or submicrometric structure gained attention of the industry due to their outstanding properties [29]. However, the smaller particles are (especially sizes lower than 5 μm), the bigger velocity of carrier gas has to be to transport particles into the plasma. This phenomena disturbs plasma stream and decreases the deposition rates [30]. In these cases the ultra-fine powder feedstock agglomerates and clogs the nozzle or it might evaporate in the plasma jet. That is why the pure powder is injected in a liquid feedstock - solution or suspension.

This method of coating deposition from liquid feedstock raised the most in 1990s due to the significant possibility of manufacturing nanostructured thick coatings with unique properties as good thermal insulation or resistance to thermal shock and wear [31].

Nowadays, both suspensions and solutions are being successfully used to form coatings by thermal spray method. Both of them are liquid mixtures of two or more components and differ physically and chemically, and so do their behaviour in plasma jet [32][30].

3.2.1 Solution

The solution is a homogeneous mixture of liquid precursors (usually inorganic salts and metallo-organic compounds) with an organic solvent such as water, ethanol or butanol [33]. The most distinctive difference from suspension is the size of particles. Solution creating particles are significantly smaller (often less than 1 nm) and have the ability to mix with solvent without any further sedimentation [32]. In the interaction of solution with plasma jet occur processes such as atomization of drops, evaporation of solvent, precipitation of solution and pyrolysis causing the heating of precursor and producing required solid particles impacting onto the substrate [30]. Liquid fragmentation of solutions depends on parameters such as the droplet size, the surface tension and boiling point of the liquid phase, the solute chemistry, its solubility and its mass diffusivity [31]. Figure 3.1 shows behaviour of plasma sprayed solution.

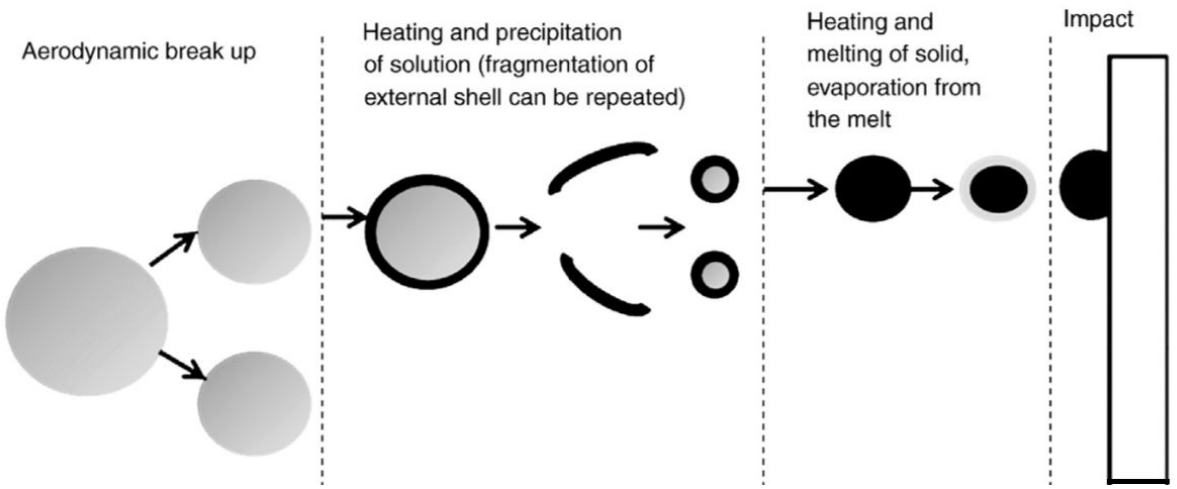

Figure 3.1: Transformation of solution droplet in the high temperature plasma jet [30]

3.2.2 Suspension

Suspensions, on the other hand, are mixture of solvent (the same as in a solution) and solid larger-size particles. The size of particles ranges between tens of nanometers and micrometers which is several times more than solution particles, but one or two orders less than pure plasma spray powders. This fact causes the inability to dissolve in solvent and sedimentation occurs [32]. The droplets of suspension penetrating the plasma jet experience processes such as the atomization of drops, vaporisation of liquid, melting and/or sintering of some fine particles, and impact onto the substrate. The sintered or melted and agglomerated particles create small lamellae or unmelted aggregates on the surface of substrate [30]. Liquid fragmentation depends on solvent, dispersing agent, solid particles mass load, particles size distribution, particle manufacturing route, particles crystallographic state [31]. The transformation of plasma sprayed suspension into a solid coating is shown in Fig. 3.2.

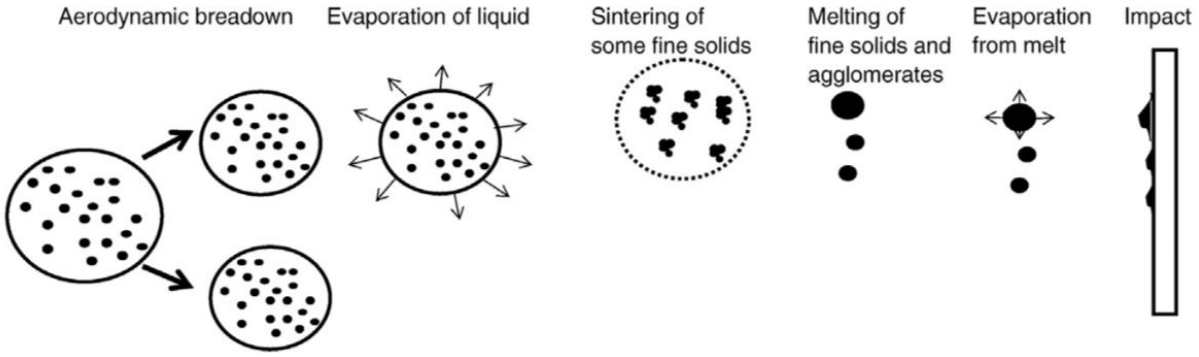

Figure 3.2: Transformation of suspension droplet in the high temperature plasma jet [30]

4 Experimental setup

This chapter describes materials, methods and devices used in the experiment, as well as the characterization techniques used to analyse the final coating properties.

4.1 Materials

4.1.1 Substrates

The task was to explore the influence of the organic carrier on the applied coating properties. Besides that, the substrate on which it is applied also has been tested as it affects the coating. Therefore, two types of substrate material were used, a structural steel S235 and a stainless steel SS304 (AISI 304).

Table 4 shows comparison of chemical composition of S235 and SS304 and Table 5 compares their material characteristics.

Table 4: Elemental composition of S235 and SS304 [34][35]

Steel	**C** [%]	**Mn** [%]	**Si** [%]	**P** [%]	**S** [%]	**Cr** [%]	**Ni** [%]	**N** [%]
S235	0.22	1.60	0.05	0.05	0.05	-	-	0.014
SS304	0.10	2.0	0.75	0.045	0.03	20.0	10.5	0.1

Table 5: Mechanical properties of S235 and SS304 [36][37]

Steel	ρ $[kg/m^3]$	E $[GPa]$	$R_{p0.2}$ $[MPa]$	UTS $[MPa]$	λ $[W/m.K]$	α $[10^{-6}/K]$
S235	7800 - 7900	200 - 215	235	360 - 510	49 - 54	11.5 - 13
SS304	8000	200	290 - 550	580 - 760	16	17

Two shapes of substrate samples were used for the experiment - rectangular 20x30 mm^2 and circular with diameter 25 mm - shown in Fig. 4.1. The rectangular samples were intended for measuring the surface roughness and embedding in resin to next processing in metallography. Those samples were then subjected to the micro-hardness test, observation and elemental analysis by EDX in scanning electron microscope (SEM) and phase analysis by X-Ray diffraction (XRD). The circular ones were created for pull-off test to find out the level of adhesion and cohesion of the coating.

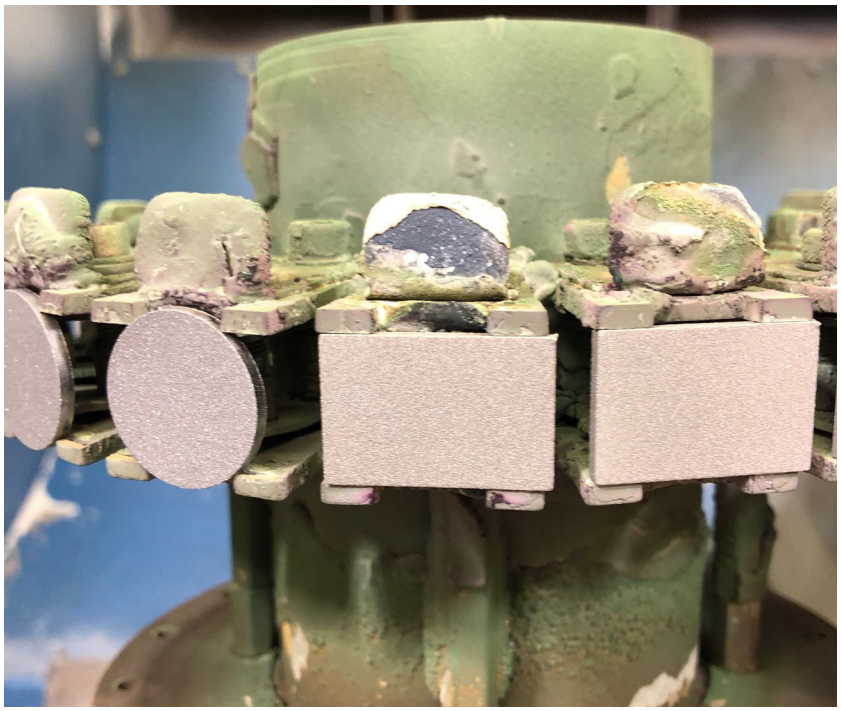

Figure 4.1: Two different sample types mounted in a revolving carousel

4.1.2 Suspensions

The suspensions composed the organic carriers ethanol or dowanol, the coating powder Al_2O_3 and dispersing additive BYK. There were prepared 3 suspensions of different concentrations and contents. The following abbreviations are introduced to simplify orientation in the further text, graphs, and tables:

- **Et10:** Ethanol + 10 $wt\%$ Al_2O_3 + 0.5 $wt\%$ BYK
- **Dw10:** Dowanol + 10 $wt\%$ Al_2O_3 + 0.36 $wt\%$ BYK
- **Dw20:** Dowanol + 20 $wt\%$ Al_2O_3 + 0.5 $wt\%$ BYK

Ethanol is a simple alcohol with a chemical formula CH_3CH_2OH and was obtained from Penta (Czech Republic), while dowanol belongs to an ether group and its chemical formula is $CH_3O[CH_2CH(CH_3)O]_2H$. It was manufactured in the USA by the Dow Chemical Company. Technical specifications of solvents are given in Table 6.

Table 6: Technical data of ethanol and dowanol [38][39]

Solvent	Boling point $[°C]$	Density $[g/cm^3]$	Viscosity $[mPa.s]$	M_r $[g/mol]$
Ethanol	78	0.79	1.2	46.07
Dowanol	190	0.953	3.7	148.2

Thermal properties of solvents are significantly different, which is why these two substrates were chosen for comparison in experiment.

Solvent fills the most of the suspension's volume, but the most essential component of the mixture is the sprayed material, in this case, an Al_2O_3 ceramic (alumina).

This particular abrasive powder with the medium particle size of 300 nm was used as the main component of the produced suspensions applied onto the substrates. Further technical information is summarised in Table 7.

Table 7: Technical data of alumina powder [40]

Additive	**Form**	**Color**	**Size** $[nm]$	**Melting point** $[°C]$	**Density** $[kg/m^3]$
Al_2O_3	powder	white	300	2050	920

The size of particles was measured using the analyser Mastersizer 3000 at the Institute of Plasma Physics in Prague and the particle size distribution graphed in Fig. 4.2 was provided by the institute scientist Ing. Tomáš Tesař.

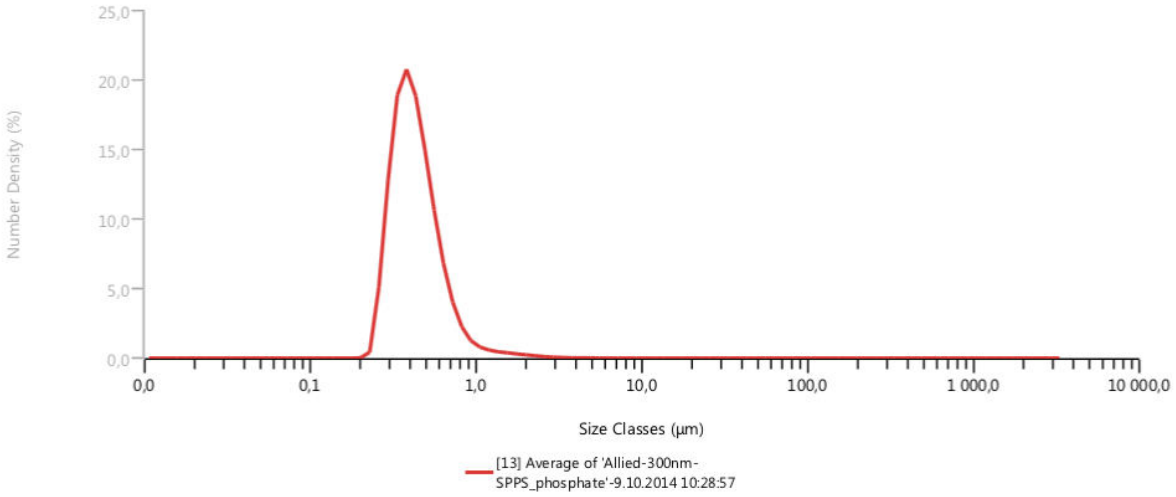

Figure 4.2: Particle size distribution of alumina powder used in the experiment

The suspension stability also affects the coating build-up which is why it must be carefully optimised to avoid sedimentation, agglomeration or flocculation and secure the constant deposition conditions [41]. Several viscosity tests were made and evaluated by rotational viscometer Brookfield DV2T. The viscosity dependence on speed is shown for each suspension in graphs pictured in Figs. 4.3 - 4.5.

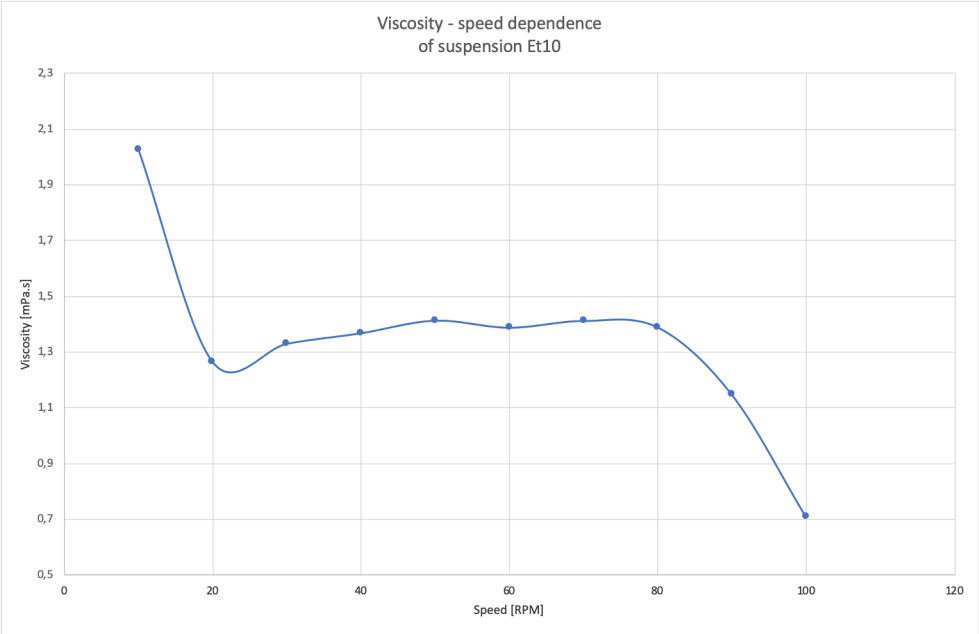

Figure 4.3: Dependence of viscosity on speed of suspension Et10

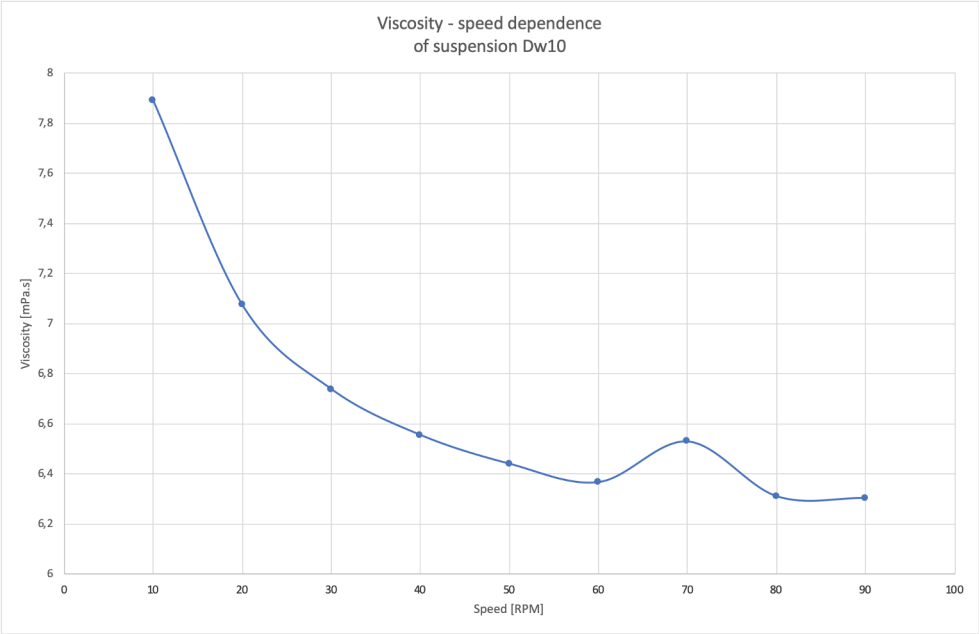

Figure 4.4: Dependence of viscosity on speed of suspension Dw10

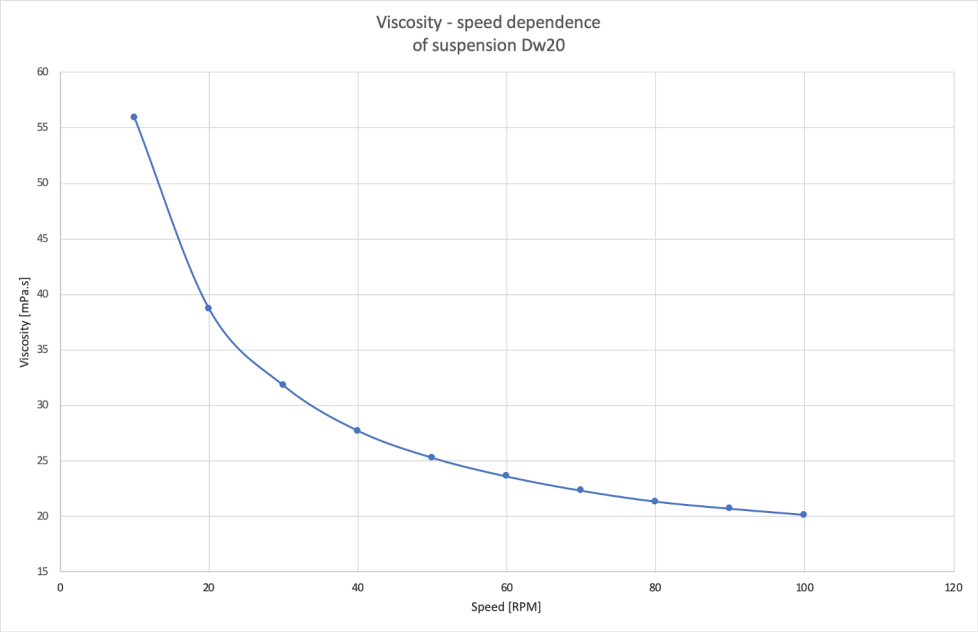

Figure 4.5: Dependence of viscosity on speed of suspension Dw20

Despite using dispersing agent BYK to avoid agglomeration or flocculation the powder is not soluble in either solvent and tends to sediment. Thereupon, the mixture was stirred properly for at least 20 minutes before spraying, filtered through a fine sieve and incessantly stirred by magnetic stirrer during the whole process of spraying.

The suspensions were dosed through a nozzle pointed to the centre of plasma jet under 25° angle. The whole setup of dosing, the feeding pressure, feed rate and spraying distance, was configured using the high speed camera providing shadowgraphy images (Fig. 4.6).

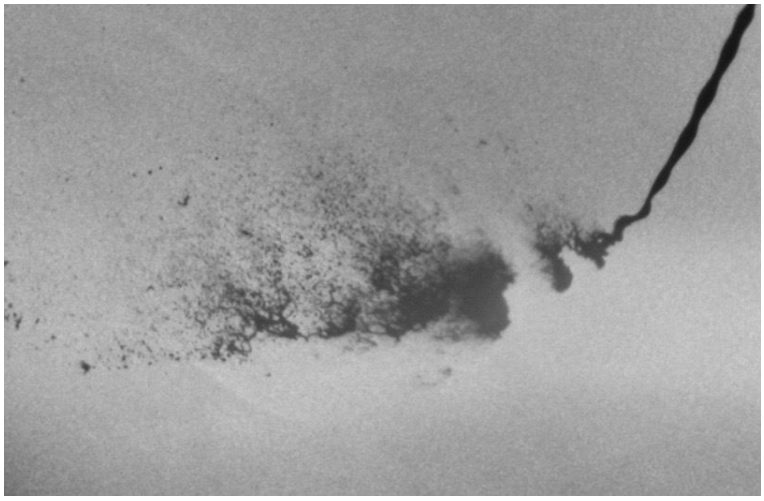

Figure 4.6: Injection of solvent to plasma jet to adjust the suspension feeding

4.2 Plasma deposition

The hybrid technology of plasma stabilised with water and argon played a key role in coatings depositions in the experiment. The torch using this technology has undeniable advantages but also associated with the assumptions that must be obeyed.

4.2.1 WSP-H

Hybrid water-stabilised plasma torch used for the substrates spraying is utilised by the Institute of Plasma Physics in Prague, Czech Academy of Sciences.

The technology of WSP-H was described in section 2.3 in theoretical part of this work. The exact specifications and machine settings set for the coatings spraying are summed up in Table 8 and Table 9. The torch (Fig. 4.7) was mounted on a robotic arm, shown in Fig. 4.8 (supplied by the ABB company) to allow controlling of spraying position and distance from substrate samples. Those were mounted onto carousel, pictured in Fig. 4.1 that serve to hold and rotate the samples to equally deposit the layers of coating onto the substrate.

Figure 4.7: WSP-H torch

Figure 4.8: Robotic arm holding WSP-H torch

Table 8: Plasma spray settings

Spray design			
Suspension	Et10	Dw10	Dw20
Solvent	Ethanol	Dowanol	Dowanol
Al_2O_3 **concentration** $[wt\%]$	10	10	20
BYK concentration $[wt\%]$	0.5	0.36	0.5
Torch type	WSP-H	WSP-H	WSP-H
Torch power $[A]$	500	500	500
Argon flow $[slpm]$	15	15	15
Spraying distance $[mm]$	100	100	100
Feeding angle $[°]$	25	25	25
Nozzle diameter $[mm]$	0.35	0.35	0.35
Feeding pressure $[bar]$	4	3.5	3
Feed rate $[g/min]$	98	100	88.95

Table 9: Carousel settings

Spray record	
Holder type	carousel
Robot speed $[mm/s]$	30
Vertical travel distance $[mm]$	15
Carousel speed $[RPM]$	55.4
Carousel frequency $[Hz]$	21.25
Preheat temperature $[°C]$	200 - 280
Spray temperature $[°C]$	250 - 550
Spraycam optimisation	yes
Et10 & Dw10 jet passes	26
Dw20 jet passes	14

4.2.2 Preparation of samples and coating deposition

Besides the perfect adjustment of plasma torch itself it is necessary to prepare substrate samples properly too. They had to be blasted to remove the oxidised layer and other surface inclusions, a process which also roughened the surface for better adhesion of deposit. Finally, the samples were immersed in acetone in laboratory ultrasonic bath Kraintek K-2LE to remove the impurities and grease residues.

Clean substrates were mounted to carousel and right before spraying they were heated up to spraying temperatures by a few passes of plasma jet without material feeding (Fig. 4.9). The temperature of plasma jet in front of carousel was observed and measured by thermal camera and the temperature of substrate samples was detected by thermo-galvanic cell placed inside the carousel and attached to one sample. The samples were constantly air cooled during the spraying.

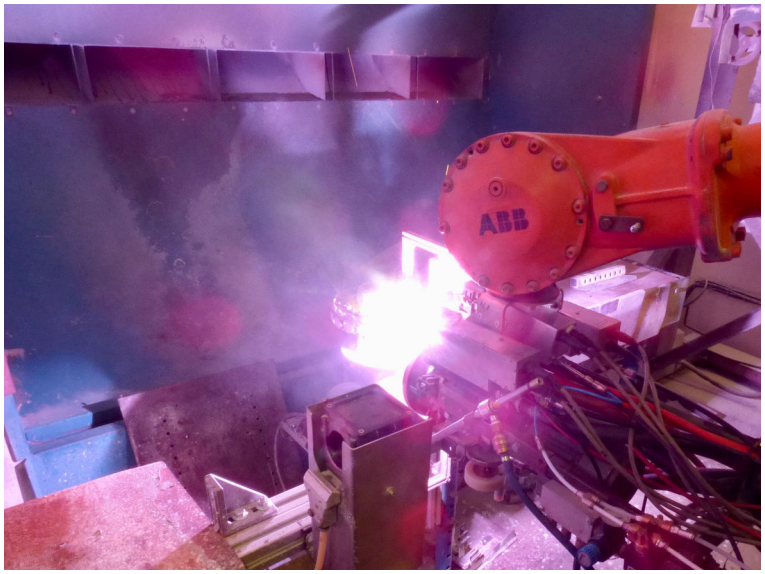

Figure 4.9: Preheating the substrates and preparation for spraying

4.3 Characterisation of samples

This section is focused on the samples analysis after the spraying process. The deposition efficiency was determined by weighing the sample before spraying and after, considering the respective number of torch passes. The coating roughnesses R_a and R_z were measured using the surface roughness tester Mitutoyo SJ-210. Five measures along the longer side and five other along the shorter one to set average values. The applied coatings on the substrates were put into the X-ray system Bruker D8 Discover diffractometer to analyse the alumina phases content using X-Ray diffraction method (XRD).

The circular samples glued to steel holders using a FM1000 adhesive (treated at 180°C for 100 minutes) and pull-off adhesion tests according to ASTM C-633 standard [42] were then carried out using testing system Instron Model 1362. The ramp rate of the machine was 0.5 mm/min. Before gluing the sprayed samples themselves, the test of glue was executed on testing cylindrical steel holders. After testing the glue adhesion, only S235 samples were glued and tested because they provided sufficiently high quality coatings for adhesion test.

After that they were cut with precise metallographic saw Struers Setocom-50 using diamond cutting disc. The cut samples were embedded in Struers EpoFix resin and hardened for 24 hours. The samples were polished on automated polishing system Struers Tegramin-25.

The polished samples were observed in scanning electron microscope (SEM) Zeiss EVO MA15 and further set of micrographs was recorded for porosity determination using image software ImageJ. The porosity was determined from 5 SEM scans from each serie at 3000× magnification. The program works on the principle of hand filling pores on the taken scan, thus, it is an individual evaluation of porosity. The Fig. 4.10 shows the red filling pores in ImageJ. The SEM had also built-in Bruker e-Flash detector which analysed the samples using Energy dispersive X-ray spectroscopy (EDX) to identify the elemental composition of coatings.

The coatings and substrates were tested on Vickers microhardness at load 0.1 kg using the Qness Micro Hardness Tester. There were applied series of 20 indents to samples for sufficient comparison and determination of coating microhardness. The dimensions of the indents were determined manually, thus, it was a subjective assessment.

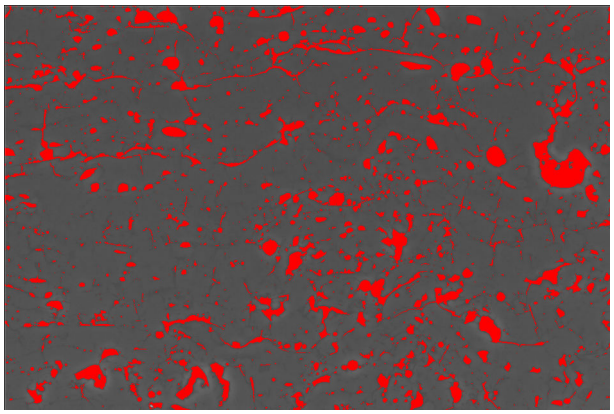

Figure 4.10: Example of ImageJ filling pores

5 Results discussion

5.1 Deposition efficiency

The suspension Et10 and the suspension Dw10 were the same, only solvents were different. Both were deposited on 26 spraying runs. The suspension Dw20 contained 2 times more solid alumina additive mixed in dowanol and was sprayed using 14 spraying runs. The calculated deposition efficiencies are shown in Tables 10 and 11.

Table 10: The deposition efficiency of each suspension on S235 substrate

S235 substrate	**Et10**	**Dw10**	**Dw20**
Coating thickness $[\mu m]$	161.1	205.1	194.9
Sample weight increase $[g]$	0.3509	0.4433	0.4074
Spraying runs	26	26	14
Per-pass thickness $[\mu m]$	6.2	7.9	13.9

The SS304 substrates were not weighed but comparable data were acquired.

Table 11: The deposition efficiency of each suspension on SS304 substrate

SS304 substrate	**Et10**	**Dw10**	**Dw20**
Coating thickness $[\mu m]$	155.3	202.2	181.7
Spraying runs	26	26	14
Per-pass thickness $[\mu m]$	6.0	7.8	13.0

Deposition efficiency between substrates S235 and SS304 has not a striking difference. Thermal conductivity (respectively the heat dissipation of substrate) makes no difference and the deposition efficiency is independent on choice of substrate. Once again, the dowanol suspension showed a little more efficient deposition than ethanol. This is promising acquisition increasing an economical part of the process. Significantly better results were achieved by spraying suspension Dw20 with more solid content of alumina which exerted two times bigger growth on both substrates.

5.2 Surface roughness

The choice of substrate did not cause any significant change between the roughnesses of coatings. Neither differences between roughnesses dependent on choice of solvent were dramatically different but dowanol suspension formed slightly rougher surface than ethanol which is consistent with SEM observation in section 5.3. However, it could be a benefit in applications demanding high specific surface. The surface roughnesses R_a and R_z were measured and set in Table 12 and Table 13 for each type of substrate material.

Table 12: The surface roughness of coatings deposited on S235 substrate

S235 substrate	**Et10**	**Dw10**	**Dw20**
R_a (length)	6.99	7.71	8.70
R_a (width)	6.13	7.87	7.81
R_z (length)	37.84	41.68	45.55
R_z (width)	33.73	41.76	40.81
R_a	**6.56**	**7.79**	**8.26**
R_z	**35.79**	**41.72**	**43.18**

Table 13: The surface roughness of coatings deposited on SS304 substrate

SS304 substrate	**Et10**	**Dw10**	**Dw20**
R_a (length)	5.68	6.35	9.25
R_a (width)	5.61	6.71	8.11
R_z (length)	33.39	35.65	47.49
R_z (width)	33.08	36.71	43.28
R_a	**5.65**	**6.53**	**8.68**
R_z	**33.24**	**36.18**	**45.39**

5.3 Microstructure

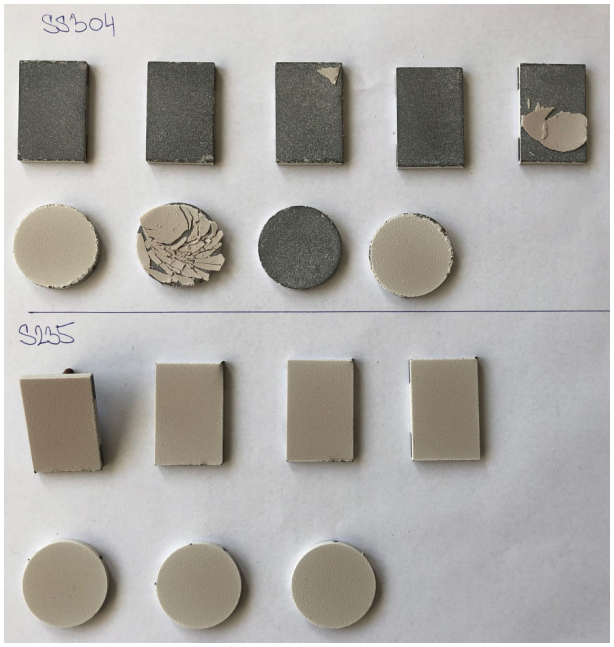

Figure 5.1: Suspension Et10 deposited on substrates S235 and SS304

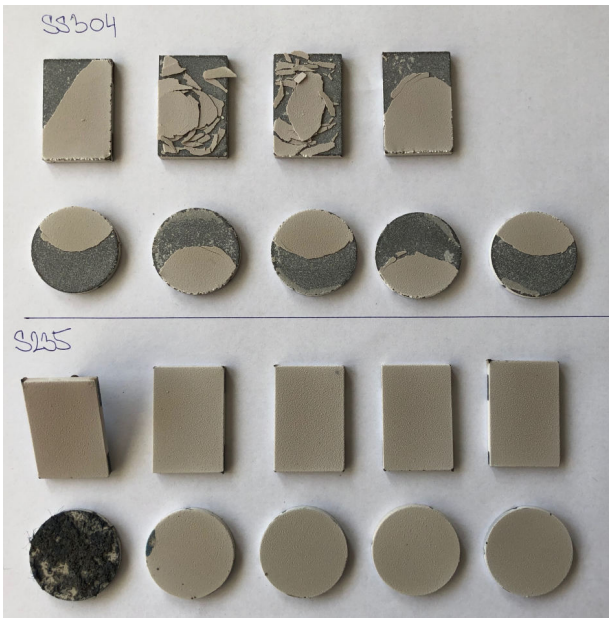

Figure 5.2: Suspension Dw10 deposited on substrates S235 and SS304

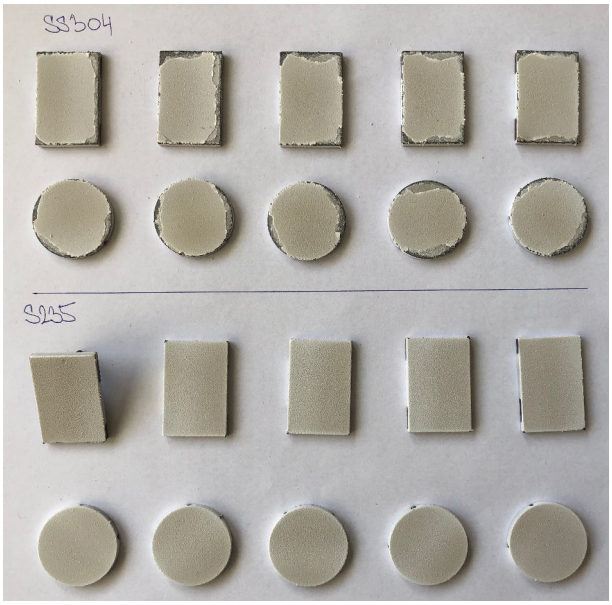

Figure 5.3: Suspension Dw20 deposited on substrates S235 and SS304

The sprayed coatings shown in Figs. 5.1 - 5.3 represent the behaviour of suspension-sprayed coatings on both substrate types. It is clearly visible, the substrate S235 causes much better adhesion and cohesion of coating than SS304. The lower number of samples for the Et10 series is caused by several samples falling away from the carousel during the spray run. Black round sample in set Dw10 fell down of the carousel and was not used for

further measurement. However, a sufficient number of samples were provided to generate general conclusions.

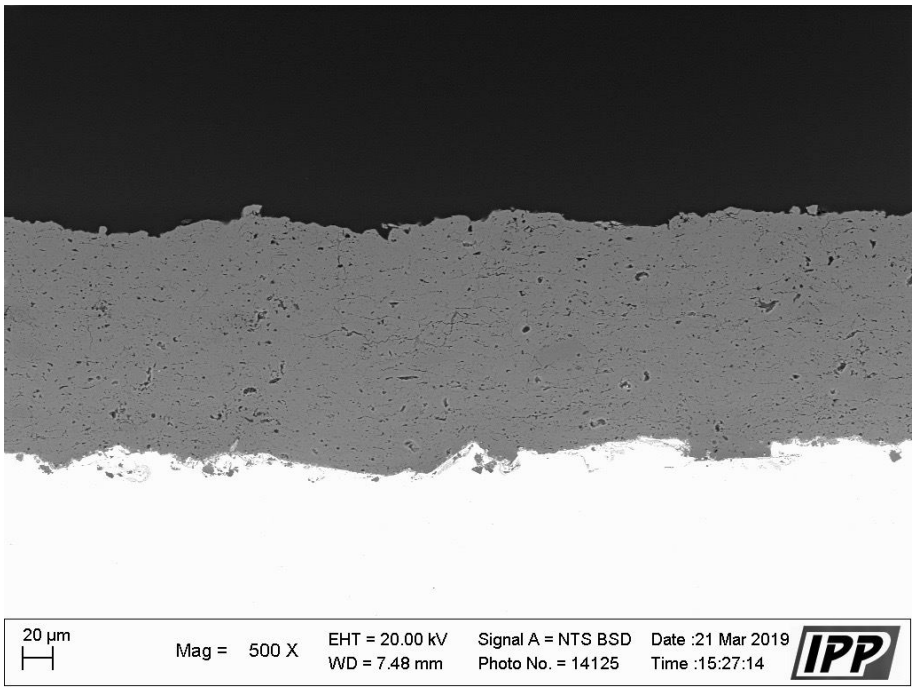

Figure 5.4: Et10 coating deposited on S235

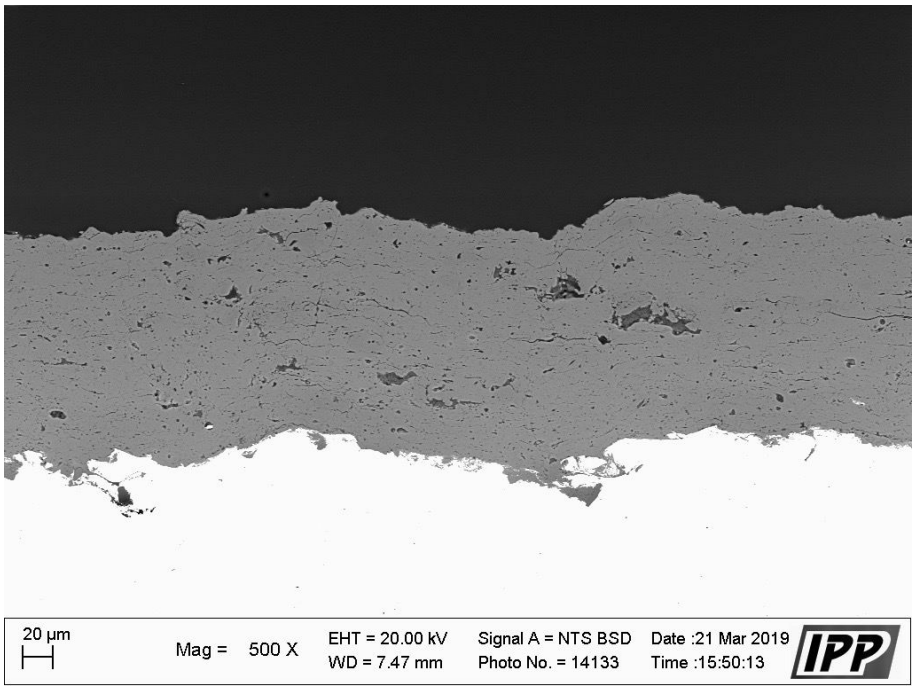

Figure 5.5: Et10 coating deposited on SS304

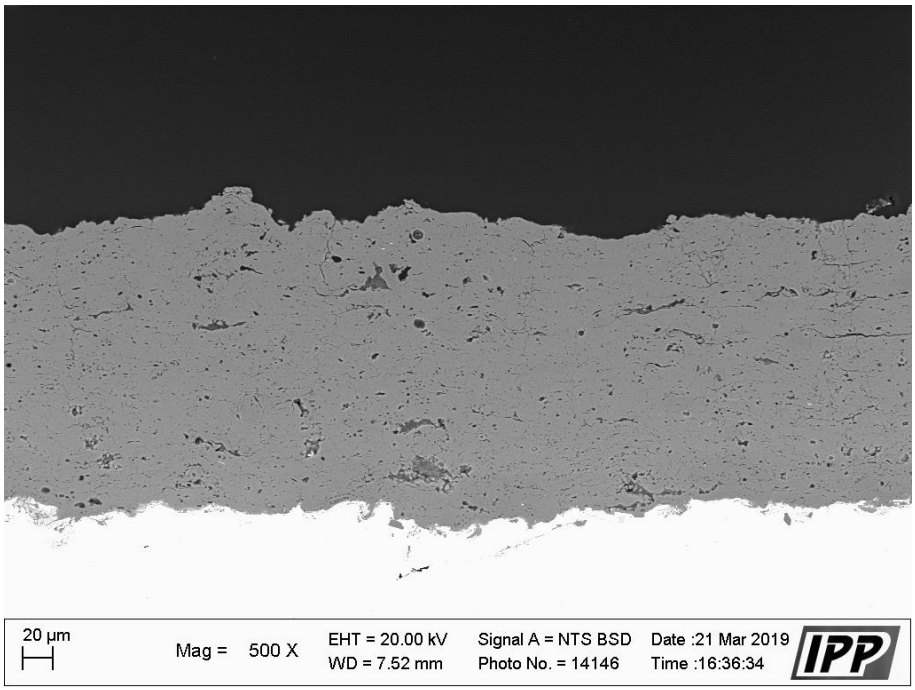

Figure 5.6: Dw10 coating deposited on S235

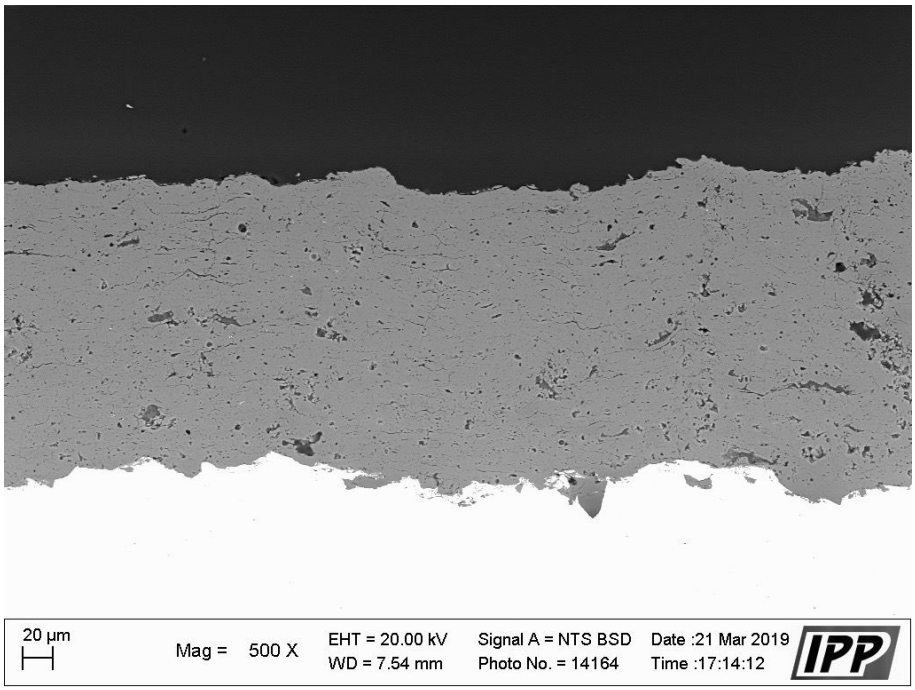

Figure 5.7: Dw10 coating deposited on SS304

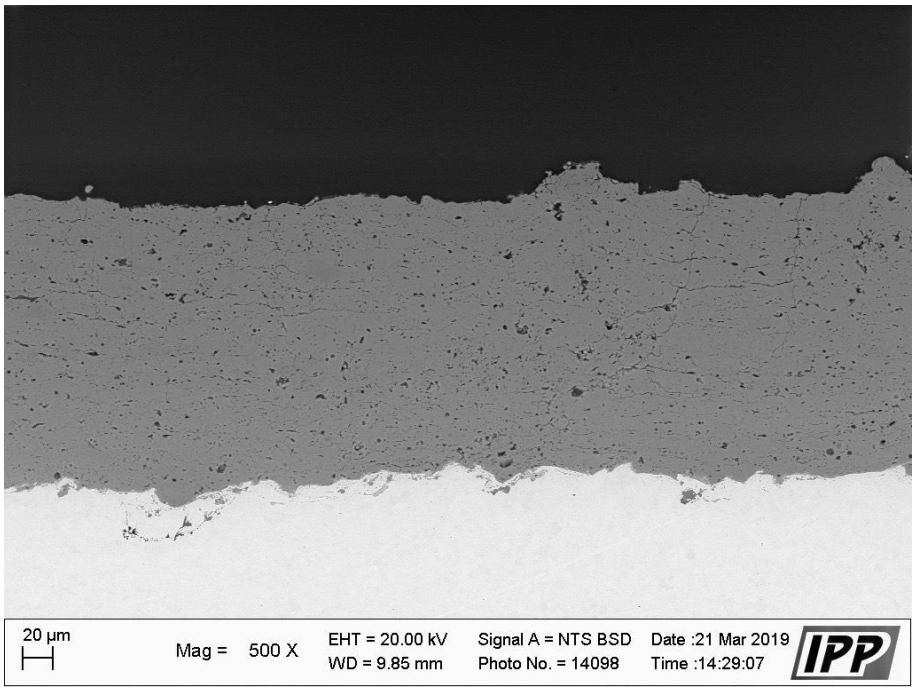

Figure 5.8: Dw20 coating deposited on S235

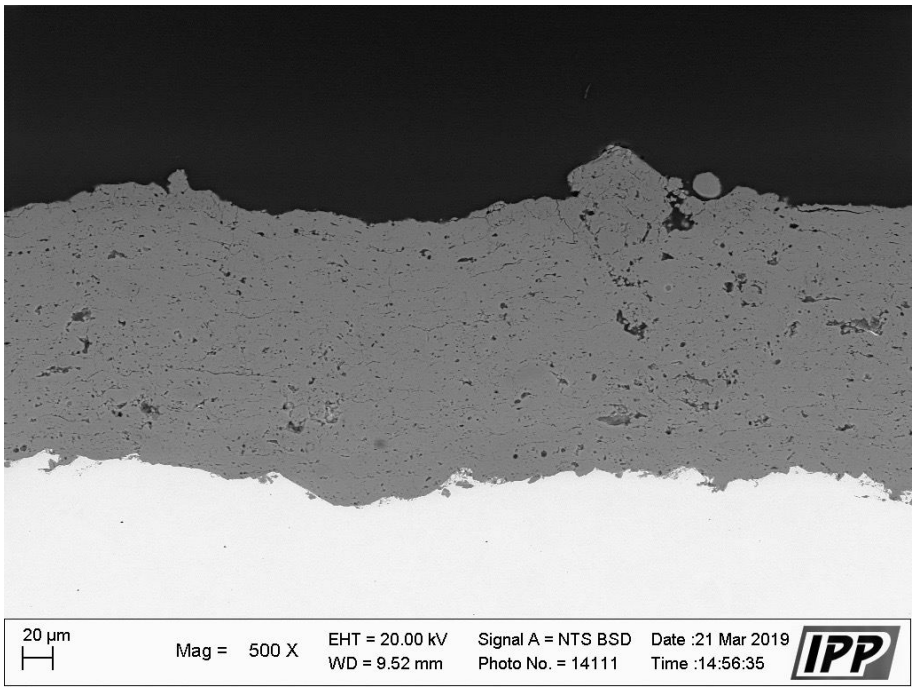

Figure 5.9: Dw20 coating deposited on SS304

The samples were observed in scanning electron microscope at several different magnifications and the resulting microstructures are shown in Figs. 5.4 - 5.9. It could be

seen that the microstructure of the three suspension-sprayed coatings does not differ significantly. The coatings appear relatively dense and contain closed porosity as well as a network of fine microcracks, typical for plasma sprayed coatings. No columnar structure often observed in suspension-sprayed coatings could be seen.

The second visible feature is deposition efficiency of dowanol suspension, discussed earlier. At the same number of passes, the Dw10 coatings are thicker than the corresponding Et10. No apparent differences in the microstructure of the three coating types are visible. This is relatively unexpected, given the different thermal properties of the two solvent types. Secondly, no significant differences were observed in the structure deposited on either steel types. This is also an unexpected result as the different properties of the substrates were anticipated to give rise to coating differences (partially exhibited by the different adhesion forces presented further in section 5.8).

5.4 Porosity

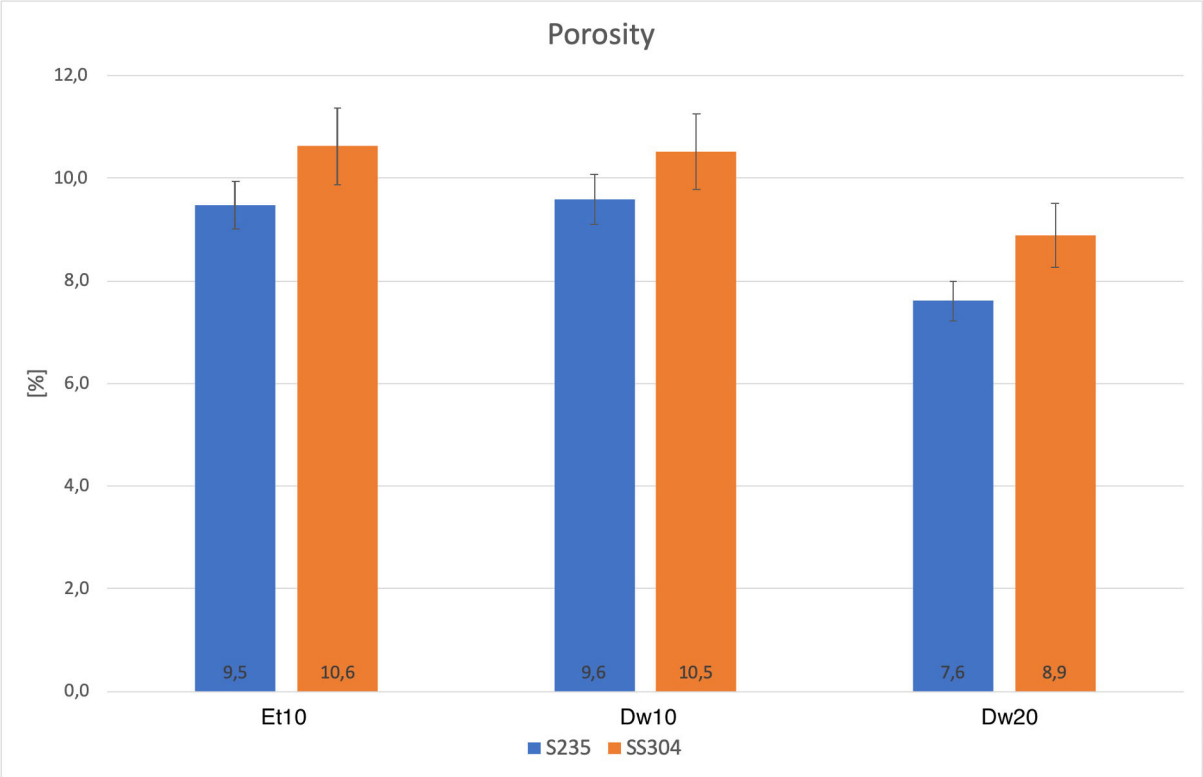

Figure 5.10: Porosity of the coatings produced from three suspension types

The porosities of deposited coatings are very similar (Fig. 5.10). The coatings on SS304 are generally more porous than on S235. Suspension Dw20 contained 2 times more solid components than the others which probably caused the lower porosity. However, the differences are comparable to the standard deviation and can therefore not be taken as statistically significant.

5.5 Coatings element composition

Energy dispersive X-ray spectroscopy (EDX) method was performed in scanning electron microscope to recognise the elemental composition of observed coating. The chemical composition of the alumina particles did not change upon dispersing in the solvents. Thus, the solvent did not chemically influence the solid additive.

However, the deposited coating was not pure alumina. Diffusion of the elements from the substrates was recorded: while for S235, iron was detected in the coatings, corrosion resistant elements such as nickel and chromium were observed in the coatings deposited onto SS304 substrates. The elemental content of suspensions was very similar and therefore Table 14 shows a range of the average values.

Table 14: The EDX composition of the coatings

Elements	**S235 coating**	**SS304 coating**
O [%]	56.3 - 57.5	55.9 - 56.6
Al [%]	38.4 - 40.2	39 - 41
Fe [%]	3.1 - 4.1	2.3 - 3.2
Cr [%]	-	0.8 - 0.9
Ni [%]	-	0.2 - 0.3

5.6 Coatings phase composition

The resulting coatings were analysed by analytical technique XRD for phase identification. The measured data corresponding to individual coatings are shown in graphs pictured in Fig. 5.11 - Fig. 5.16. One of the advantages of using dowanol instead of ethanol as the solvent in suspension with Al_2O_3 was to form a coating with higher content of α-phase alumina.

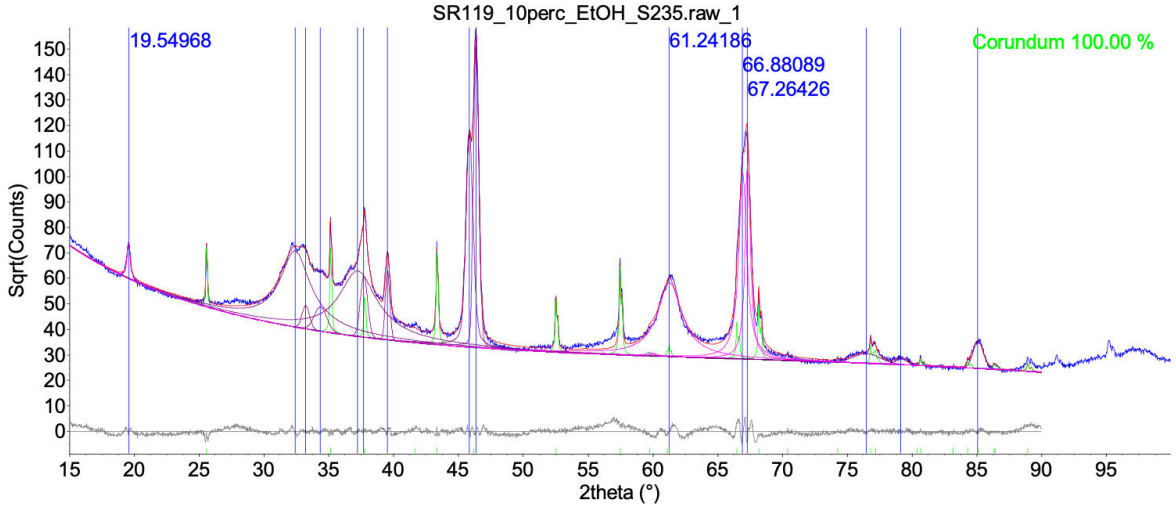

Figure 5.11: XRD of suspension Et10 on S235 substrate

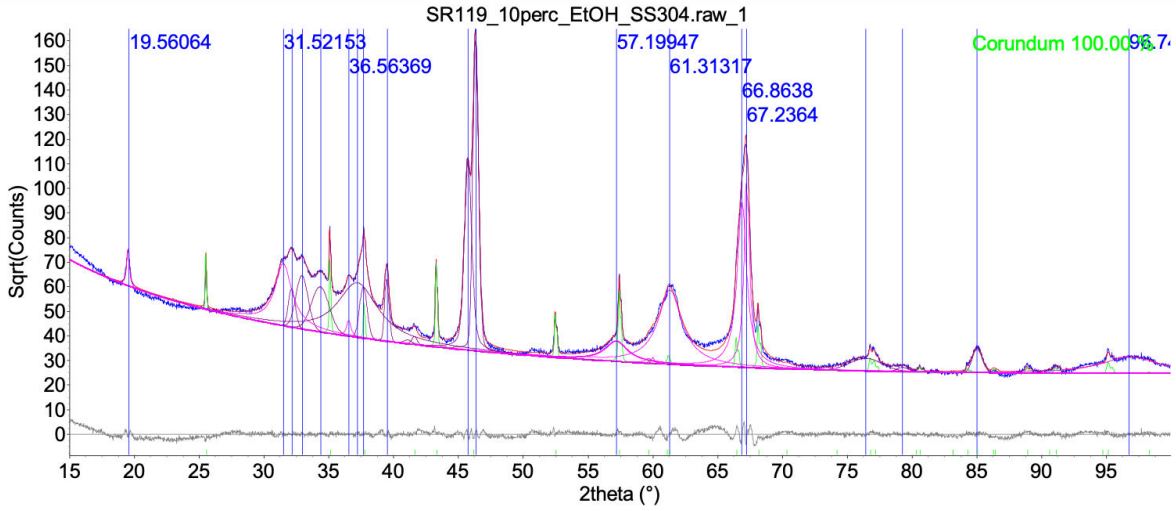

Figure 5.12: XRD of suspension Et10 on SS304 substrate

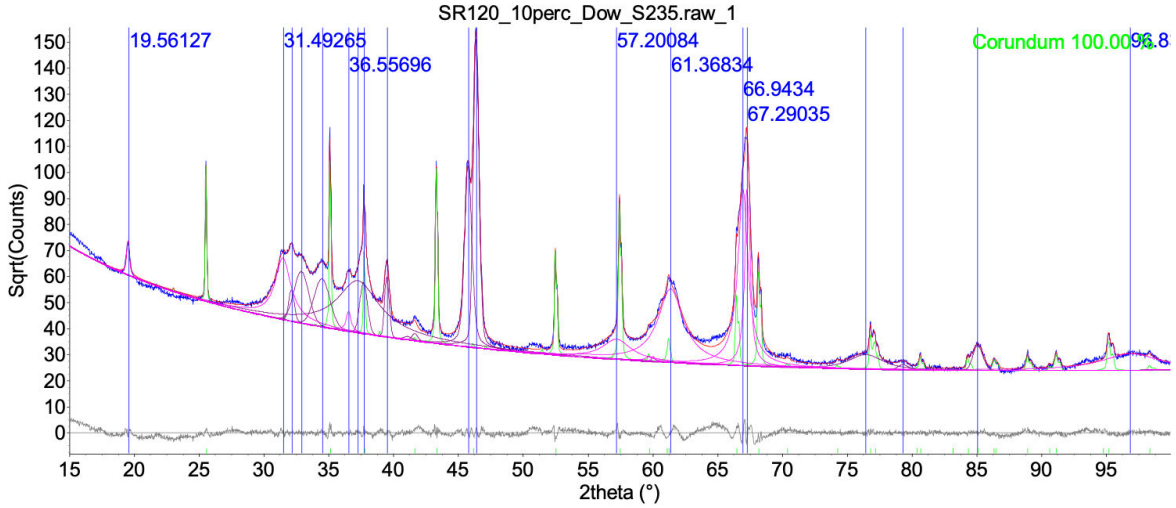

Figure 5.13: XRD of suspension Dw10 on S235 substrate

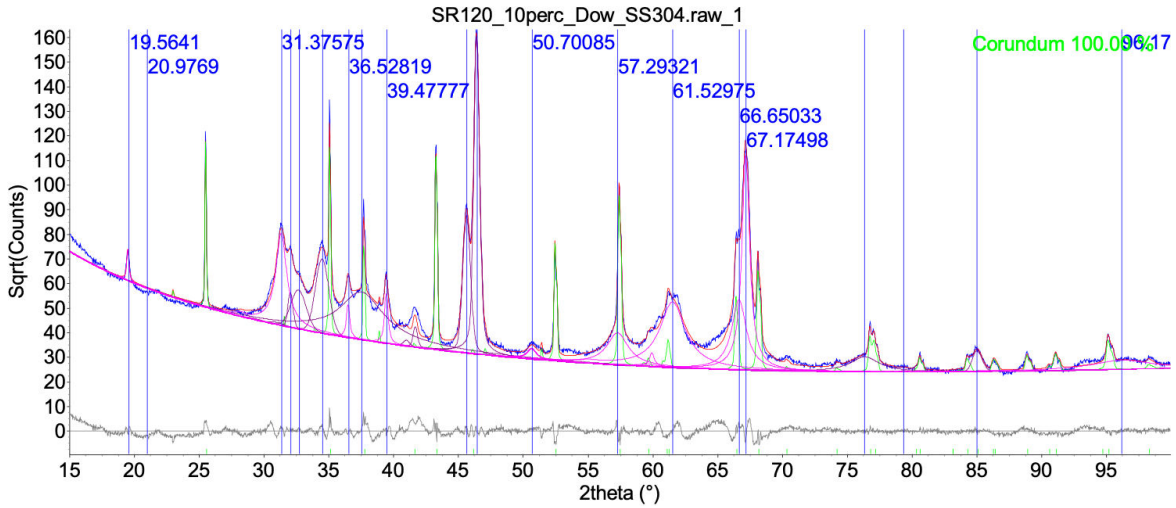

Figure 5.14: XRD of suspension Dw10 on SS304 substrate

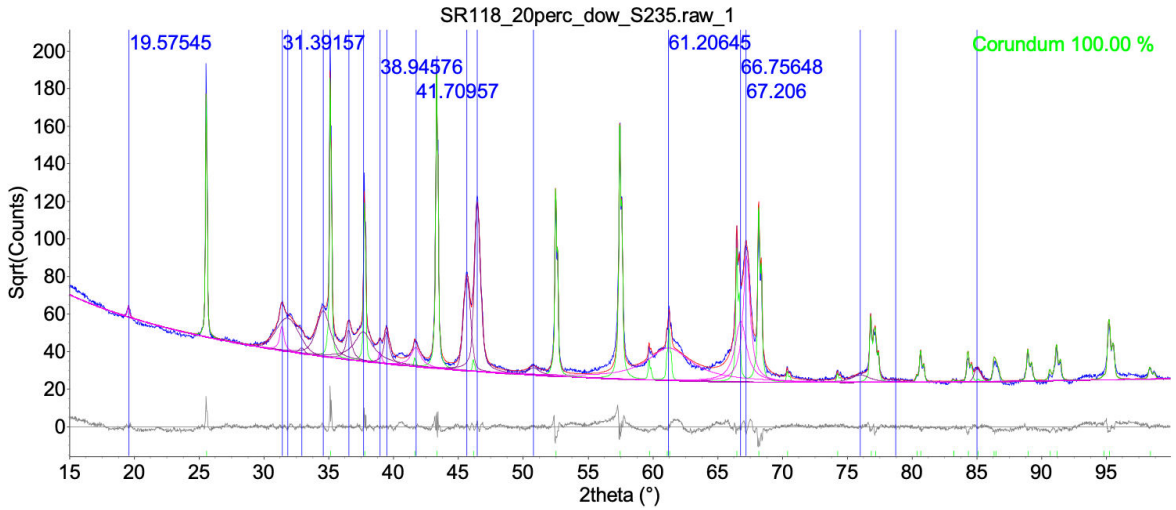

Figure 5.15: XRD of suspension Dw20 on S235 substrate

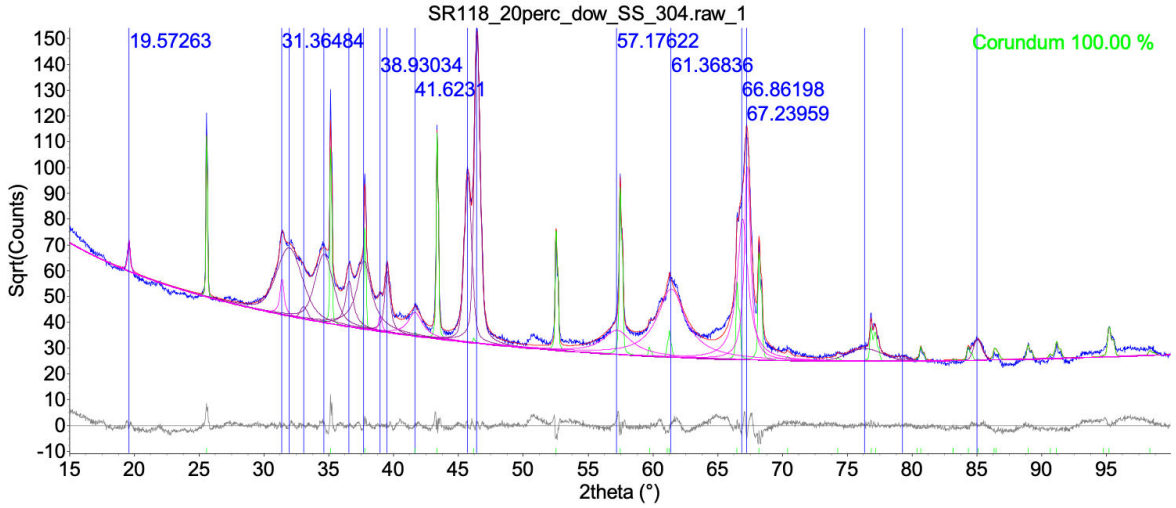

Figure 5.16: XRD of suspension Dw20 on SS304 substrate

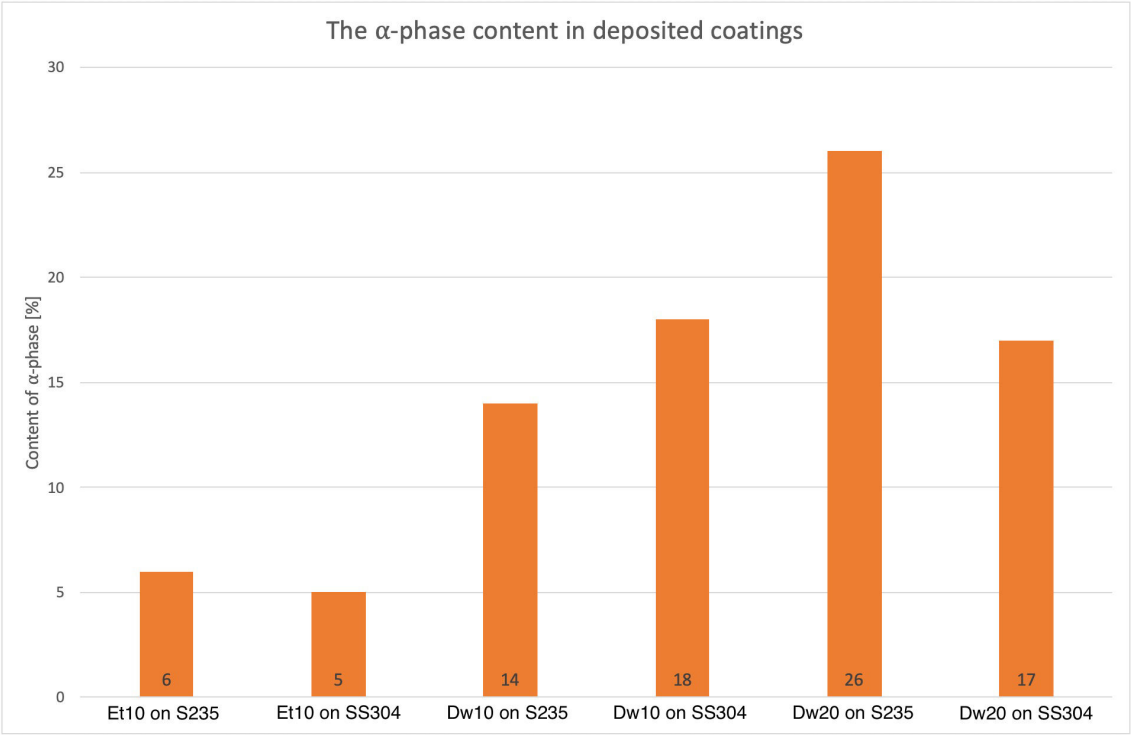

Figure 5.17: The α-phase content in applied coatings

The summarised data from XRD analysis are in Table 15 and visually in Fig. 5.17 which prove dowanol's qualities. The suspension Dw10 comparable with suspension Et10 demonstrated its ability to retain at least two times higher content of the α-phase alumina, probably due to thermal properties of dowanol. The suspension Dw20 kept 26 % of α-phase alumina on S235 substrate which is the best result of all tested suspensions opening new possibilities for further research.

Table 15: Phase content of Al_2O_3 coatings produced from suspensions Et10, Dw10, Dw20

	Et10 S235	**Et10 SS304**	**Dw10 S235**	**Dw10 SS304**	**Dw20 S235**	**Dw20 SS304**
α**-phase** [%]	6	5	14	18	26	17
γ/δ**-phase** [%]	94	95	86	82	74	83

5.7 Microhardness

The Vickers microhardness was tested on substrates and coatings at load 0.1 kg and collected data are shown in Table 16.

Table 16: Vickers microhardness of coatings and substrates

Substrate	**Et10**	**Dw10**	**Dw20**	**Substrate**
S235 [$HV0.1$]	1657	1889	1684	138
SS304 [$HV0.1$]	1643	1962	1863	198

The dowanol suspensions formed harder coatings than ethanol. The exact mechanism of hardness difference is yet to be understood. But the choice of substrate probably played a role this time but definite explanation is not known without further research.

5.8 Adhesion test

The samples were tested for coating's adhesion/cohesion. The results of glue and coatings adhesion are shown in Table 17.

Table 17: Pull-off test of coatings adhesion on S235 substrate

Pull-off	**Et10**	**Dw10**	**Dw20**	**Glue**
Adhesion [MPa]	59>	29	25	74

In the case of Et10 suspension, all samples ruptured at the glue rather than at the coating. All samples were pulled-off on the interface between the glue and the gripping body at load 59 MPa. Therefore, it can be assumed the coating itself will last more which also can be confirmed on the basis of Ing. Tomáš Tesař's previous research of spraying ethanol + 10% Al_2O_3.

The reason of the inferior adherence of the Dw10 and Dw20 coatings is not known at the moment. It may reside in the somewhat rougher surface of the coatings, which could potentially lead to a cohesive rupture rather than whole coating detachment. However, a further research is needed (fractography of the ruptured surfaces) to better understand the phenomenon.

The spallation of the coatings off the SS304 substrates as opposed to their superior adherence on S235 could be caused by the different thermal properties of the two steels, in particular the notably lower thermal conductivity of the SS304 and, most importantly, its higher coefficient of thermal expansion.

6 Conclusion

This work was theoretically concerned with methods of thermal spray and especially with the hybrid water-stabilised plasma method, which was used in the experimental setup. Part of literature review was devoted to the coatings, their composition, and shortly to a section of the alumina powder that formed the solid component of the suspensions. The application of coatings from the suspension is a trend of recent years which has opened up new possibilities of applying nano-particle powders. The purpose of this bachelor thesis was to compare the influence of the solvent type on the properties of suspension plasma-sprayed Al_2O_3 coatings surveyed in experiment.

The research confirmed the impact of the solvent on the final coating properties. The solvent caused the different coating thicknesses, porosities, and presumably the adhesion and cohesion, and the hardness. The content of the α-phase of alumina coating could be influenced by the substrate. The substrates differed in another heat dissipations and the temperature change has an impact on the amount of the α-phase formed in the coatings.

At the moment, it indeed seems that dowanol may be a promising solvent choice for deposition of polymorphic oxide-based ceramics due to its superior thermal properties over ethanol. Further studies using other materials are planned to study this interesting opportunity.

In a direct comparison with ethanol-based suspension, the final coatings exhibited several improved characteristics (except for adherence). The dowanol-based suspensions are great for applications requiring the sufficient hardness and higher deposition efficiency while the adhesion and cohesion of the coating is not a focus of interest.

Dowanol benefits:

- Deposition efficiency
- Higher content of α-phase alumina
- Hardness

Ethanol benefits:

- Higher adhesion/cohesion

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7 List of abbreviations and symbols

Abbreviations

APS	Atmospheric plasma spray
ASTM	American society for testing and materials
CVD	Chemical vapor deposition
DC	Direct current
D-Gun	Detonation gun
EDX	Energy-dispersive X-ray spectroscopy
HCP	Hexagonal close packed
HVAF	High velocity air fuel
HVOF	High velocity oxygen fuel
LPPS	Low pressure plasma spray
MAPP	Methyl-acetylene-propadiene
PVD	Physical vapor deposition
SEM	Scanning electron microscope
UTS $[Pa]$	Ultimate tensile strength
VPS	Vacuum plasma spray
WSP-H	Hybrid water-stabilised plasma
XRD	X-Ray diffraction

Symbols

α $[10^{-6}/K]$	Thermal expansion
E $[Pa]$	Youngs's modulus
λ $[W/m.K]$	Thermal conductivity
M_r $[g/mol]$	Relative molecular mass
ρ $[kg/m^3]$	Density
R_a $[\mu m]$	Mean roughness
Rp0.2 $[Pa]$	Offset yield strength
R_z $[\mu m]$	Mean roughness depth